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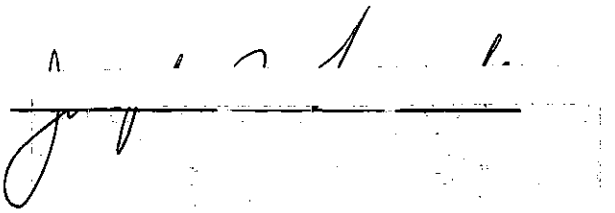

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# THE MECHANISM OF THE ADDITION REACTION OF TRIMETHYLALUMINUM WITH BENZOPHENONE

A THESIS

Presented to

The Faculty of the Graduate Division

by

Joseph Thomas Laemmle

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemistry

Georgia Institute of Technology

June, 1968

THE MECHANISM OF THE ADDITION REACTION

OF TRIMETHYLALUMINUM WITH BENZOPHENONE

Approved:

Chairman

Date approved by Chairman: April 8, 1968

## ACKNOWLEDGMENTS

The author wishes to thank Dr. E. C. Ashby, who suggested the problem, for his guidance throughout the course of this work. The mathematical aid given by Dr. H. M. Neumann is greatly appreciated. The author also wishes to thank F. W. Walker for his aid in maintaining the type of inert atmosphere box necessary to make accurate measurements on dilute organoaluminum compounds.

Financial assistance by the Georgia Institute of Technology and the Alfred P. Sloan Foundation is gratefully acknowledged.

The author also wishes to express his gratitude to his wife, Pat, for her patience and perseverance in putting this thesis in its proper form.

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# SUMMARY

The reaction of trimethylaluminum with benzophenone was studied in both benzene and diethyl ether.

When trimethylaluminum is allowed to react with benzophenone in benzene only one methyl group is available for reaction. The only product formed is 1,1-diphenylethanol. The side reactions of enolization and reduction are eliminated by the choice of ketone and aluminum alkyl. In the first successful kinetic study reported the reaction was found to proceed through two mechanisms depending upon the aluminum alkyl to ketone ratio. In both cases the reactants immediately form a complex whose formation is governed by a very large equilibrium constant. When the aluminum alkyl to ketone ratio is 1:1 or less, the product is formed by a relatively slow decomposition of the complex. The kinetic expressions in this case are complicated by the fact that the initial dimethylaluminum carbinolate formed can further complex trimethylaluminum. When excess trimethylaluminum is allowed to react with benzophenone the preferred mechanism becomes operative. The complex initially formed is rapidly attacked by monomeric trimethylaluminum to give the product.

The reaction of trimethylaluminum with benzophenone in ether is extremely slow because the amount of complex formed is very small. More data is needed on this reaction in ether to draw mechanistic conclusions.

# CHAPTER I

# INTRODUCTION

## Background

The nature of organoaluminum compounds and their reactions with olefins to catalyse polymerization have been the subject of considerable study. Until recently, however, the reactions of organoaluminum compounds with ketones, esters, and aldehydes have been largely ignored. The reactive organoaluminum species in these reactions and the details of the reaction mechanisms are unknown.

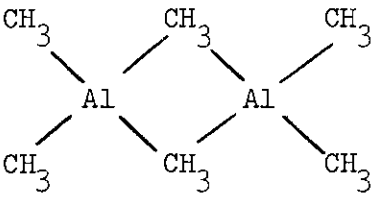
### Structure of Organoaluminum Compounds and the Nature of the Reactive Species

The structure of organoaluminum compounds in solution varies greatly depending upon the solvent. Mole[1] has shown through ebulliometric studies that a two percent solution of triphenylaluminum in diethyl ether is monomeric. Recent nuclear magnetic resonance work by Ashby[2] and co-workers indicates that trimethylaluminum also is monomeric in ether.

In hydrocarbon solvent the structure of organoaluminum compounds is quite different. Mole[1] reported that a two percent solution of triphenylaluminum in benzene is 80 percent associated. Pitzer and Gutowsky[3] studied the association of several aluminum alkyls in benzene. The concentration range reported was 0.15 to 0.67 molal in aluminum alkyl. They found tri-isopropylaluminum to be monomeric in benzene, but trimethylaluminum, triethylaluminum, and tri-n-propylaluminum were largely associated.

Definite dissociation was found in the case of triethylaluminum and tri-n-propylaluminum but trimethylaluminum was completely dimeric. In the case of trimethylaluminum if one assumes that as much as two percent dissociation could have been detected at the lowest concentration used (about 0.15 molal), then the equilibrium constant, $K_D$, for the dissociation of dimeric trimethylaluminum into monomer must be less than $2 \times 10^{-4}$.

Pitzer[4] proposed a bridge structure for the trimethylaluminum dimer in hydrocarbon solution. This structure was consistent with the infrared spectrum of this compound.




This structure is also definitely present in the solid state, as shown by x-ray techniques[5].

Recent nuclear magnetic resonance studies by Muller[6], Ashby[2], and Brown[7] show that trimethylaluminum in hydrocarbon solvent gives a single proton resonance at room temperature. As the temperature is lowered the signal shifts and broadens. At temperatures of $-65^{\circ}C$ and lower, two separate signals are found. These correspond to the protons of the bridging and terminal methyl groups. These results show that the trimethylaluminum dimer is undergoing very rapid exchange of terminal and bridging methyl groups at room temperature.

Further evidence on the liability of the organoaluminum dimer is shown by the fact that when two aluminum alkyls are mixed a rapid exchange

of alkyl groups occurs[8,9]. Mole[10] reports that triphenylaluminum exchanges rapidly with trimethylaluminum, the exchange in ether being 50 percent complete in a tenth of a second. In non-polar solvents[6] the rate is several powers of ten faster.

There is no doubt that the dimeric species of trimethylaluminum is the principal one present in hydrocarbon solution. Since dissociation to monomer and recombination is thought to be the mechanism for rapid exchange of alkyl groups[7], it is equally clear that each dimer, as a stable entity, is very short lived. This indicates that although the amount of monomer present at any instant is very small a very large amount of monomer is available for reaction in a relatively short period of time.

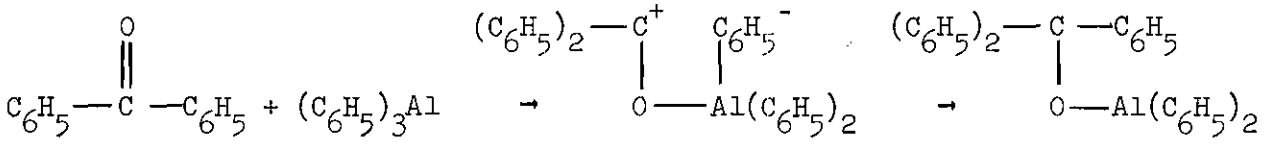
Monomeric molecules, because of the electron deficiency of the aluminum atom, would be expected to be far more reactive than their dimeric counterparts. Ziegler[11] has suggested that the monomeric form of triethylaluminum is the active species in the commercially important reaction of ethylene and triethylaluminum. A kinetic study by Smith[12] has shown Ziegler to be correct. The active species is indeed monomeric triethylaluminum.

In view of the fact that no detailed kinetic study involving aluminum alkyls other than Smith's[12] has been reported, it seems reasonable to assume that either monomer or dimer or both may be the active organoaluminum species.

The Organoaluminum-Ketone Complex

Complexation between reacting species has been suggested as the pathway to products in the reactions of organoaluminum compounds with ketones. Wittig[13] reports that the reaction of triphenylaluminum with

benzophenone proceeds through a yellow colored complex which forms immediately upon mixing the two reactants and gradually fades away. The mechanism suggested by Wittig[14] is a stepwise reaction via complex followed by migration of an anionically activated phenyl group.



Yellow Complex

Mole[15] reports that triphenylaluminum and benzophenone in benzene at room temperature form a stable yellow complex which does not react further. Upon removal of the solvent a yellow oil is obtained which gives unchanged benzophenone upon hydrolysis, but upon heating yields triphenylcarbinol. Mole suggests that the composition of the complex is $(C_6H_5)_3Al \cdot OC(C_6H_5)_2$.

The reaction of triphenylaluminum with benzophenone in boiling benzene proceeds normally through a bright yellow complex[15] to yield triphenylcarbinol. Ebulliometric measurements show that the triphenylaluminum-benzophenone complex is monomeric but gives rise to a dimeric product in about five minutes[15].

The phenylation of benzophenone in ether does not occur even after two hours reflux[15].

The reaction of trimethylaluminum with benzophenone in benzene proceeds through a yellow complex. Ebulliometric measurements show that when trimethylaluminum is reacted with benzophenone the immediate formation of a monomeric complex occurs. This reacts to give a dimeric product in about five minutes[16]. Mole[16] also reports that the reaction of

dimethylphenylaluminum with benzophenone proceeds via a monomeric complex.

Thus, the fact that the reaction between organoaluminum compounds and benzophenone proceeds via complexation appears well substantiated. In order to arrive at the correct kinetic expression for reactions of this type it is necessary to know both the stoichiometry of the complex and the equilibrium constant governing its formation. Mole[15,16] presents strong evidence that the stoichiometry of the complex is 1:1. Mole also indicates the equilibrium lies completely in favor of the complex. From Mole's ebulliometric data no free organoaluminum compound or free ketone could be found once the two were mixed in refluxing benzene. Mole admits, however, that due to the nature of organoaluminum compounds his resultant error in ebulliometric measurements may be as large as ten percent[1]. Therefore, while Mole has shown that the equilibrium lies largely in favor of the complex, he has not shown that the equilibrium completely favors the complex.

The Extent of the Reaction

In the reaction of organoaluminum compounds with ketones it is very important to establish the extent of the reaction. An alkyl or aryl aluminum compound has three groups available for possible reaction. In a kinetic study it is extremely important to determine if one or more of these groups react. If more than one group reacts then the kinetics will become quite complex due to competing reactions.

Gilman and Marple[17] found that all three aryl groups of a triarylaluminum were available for reaction with benzaldehyde, benzophenone, and benzonitrile, and the expected products were obtained in low yield. Mole[15] reports that only two phenyl groups are available for reaction when tri-

phenylaluminum is allowed to react with benzophenone. The second phenyl group was found to react much more slowly than the first. Ziegler[11] has pointed out that in the reaction of aluminum alkyls with ketones only one alkyl group is available for reaction. Mole[16] reports that in the reaction of trimethylaluminum with benzophenone only one methyl group reacts. He cites both ebulliometric data and product yield as proof.

In view of these facts the system trimethylaluminum and benzophenone appears ideal for a kinetic study. Because of the importance of being certain that only one methyl group reacts, we repeated the reaction of trimethylaluminum with excess benzophenone under conditions much more vigorous than those which Mole reports.

Kinetics and Reaction Mechanism of Organoaluminum Compounds

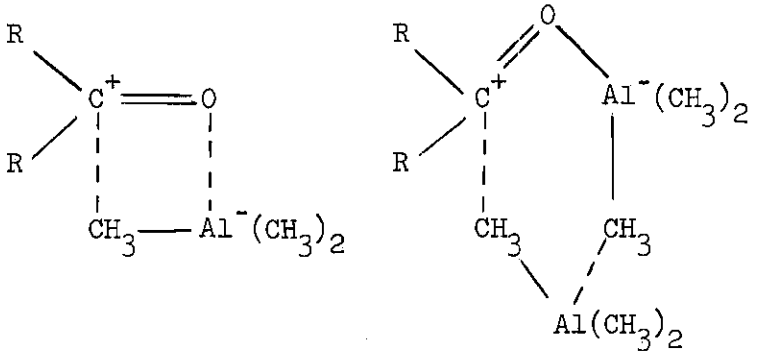
Kinetic work in the field of organoaluminum compounds is quite meager. The work of Smith[12] has already been mentioned. Mole[16] studied kinetically the reactions of benzophenone with trimethylaluminum, triphenylaluminum, and tri-isobutylaluminum in benzene. The kinetic method used included quenching the samples in ten percent hydrochloric acid and following the disappearance of the benzophenone maximum at 345 mμ by ultraviolet spectroscopy.

A kinetic examination[16] of the reaction of benzophenone with triisobutylaluminum showed the reaction to be immeasurably fast. It is almost complete after one minute at $1^{\circ}$ - $2^{\circ}$C. The reaction of triphenylaluminum with benzophenone is too fast to measure at $50^{\circ}$C. Attempts to obtain results at lower temperatures were frustrated by a strong absorption in the region of the ketone maximum.

The results that Mole[16] obtained with trimethylaluminum and benzo-

phenone are somewhat more interesting. At 50°C the reaction was found to have a half life of ten minutes when the stoichiometry of trimethylaluminum and benzophenone was 1:1. Log absorbance plots showed that the reaction is not first- or second-order with respect to the complex $(C_6H_5)_2CO \cdot Al(CH_3)_3$. A 2:1 ratio of trimethylaluminum to benzophenone resulted in an immeasurably high reaction velocity at 50°C. When the ratio $(CH_3)_3Al:(C_6H_5)_2CO$ is 1.3:1 the effect is seen in a definite acceleration in initial rate, but not in acceleration throughout the reaction. Mole concludes that the reaction is kinetically complex but gives no rate equation or data which the reaction might follow.

Pasynkiewicz and Arabas[18] studied the reaction of neat trimethylaluminum with propiophenone and methylethylphenylcarbinol was found as the sole reaction product. The yield of reaction product was found to be dependent upon the molar ratio of the reactants. The yield reaches 100 percent when the molar ratio $(CH_3)_3Al$:ketone is equal to 2:1. They proposed that rearrangement of the reaction complex for the reactant ratio 1:1 goes via a four-centered transition state and for the reactant ratio 2:1 via a six-centered transition state in which participation of dimeric trimethylaluminum was assumed.



Pasyniewicz and Sliwa[19] studied the reaction of neat triethylaluminum with diethyl ketone at several triethylaluminum to ketone ratios. As the ratio of triethylaluminum to diethyl ketone was increased the yield percent of addition product increased and the yield percent of reduction product decreased. The yield percent of enolization product was essentially independent of reactant ratio. Thus, at a ratio of triethylaluminum to diethyl ketone of 1:1, the ratio of addition product to reduction product was 2.15:1. At a ratio of triethylaluminum to diethyl ketone of 2:1, the ratio of addition product to reduction product was 4.3:1. The observation that as the ratio of addition product to reduction product is increased as the aluminum alkyl to ketone ratio is increased is cited as further evidence that a six-centered mechanism is the preferred mode of addition of aluminum alkyls to ketones.

## Purpose

In an attempt to resolve the mechanism by which organoaluminum compounds undergo normal addition reactions to ketones, a study of the reaction of trimethylaluminum with benzophenone in ether and in benzene was undertaken. A major part of this study is a kinetic investigation of the reaction in benzene.

## Approach

The reaction of trimethylaluminum with benzophenone was studied in both ether and benzene. The principal tool used in this investigation was ultraviolet spectroscopy. The ketone and complex spectra were studied thoroughly in both solvents. In addition, product studies in both solvents were made.

The kinetic study was carried out in benzene because this solvent is the one used by most previous workers who have studied organoaluminum compounds. In addition, benzene is inert to both trimethylaluminum and benzophenone whereas a polar solvent would definitely affect trimethylaluminum.

Trimethylaluminum was chosen as the organoaluminum compound for the kinetic study because it has two obvious advantages. First is the fact that trimethylaluminum is incapable of reduction thereby avoiding the reduction side product. Secondly, trimethylaluminum is reported to have only one methyl group available for reaction with ketones which simplifies the kinetics considerably. Benzophenone was the ketone of choice for several reasons. It is readily available and easily purified either by recrystallization or distillation. In addition, benzophenone is incapable of enolization which would complicate the kinetics.

# CHAPTER II

# EXPERIMENTAL

## Apparatus

### Instrumentation

A Cary Model 14 recording spectrophotometer was used for recording all ultraviolet spectra. A Zeiss PMQ II single beam spectrophotometer was used for obtaining Beer's Law plots and making kinetic measurements.

For product analysis F & M Scientific Company's Gas Chromatograph Model 750 was employed in conjunction with matched SE-30 or Carbowax 20-M columns.

### Glassware

Matched quartz, 10-mm cells (Beckman Scientific Company) were used for obtaining ultraviolet spectra.

Calibrated syringes equipped with stainless steel needles were used for transfer of reagents. Deliveries could be reproduced with an average of five parts per thousand.

Specific glassware for certain reactions will be discussed later.

### Inert Atmosphere Box

Kewaunee, Model 2C1020, was employed.

### Temperature Control

Water from a Huake constant temperature recirculator was pumped through the jacket of the Zeiss cell compartment for reactions run in the cell itself to control the temperature ($\pm$ 0.1$^{\circ}$C). For reactions in which

quenching techniques were used, a Sargent constant temperature water bath was employed for controlling the temperature (± 0.02°C). Temperature readings were made using a calibrated thermometer reading to 0.1°C (estimates possible to 0.02°C).

Timer

A Precision Scientific Company electric stopwatch reading to one-tenth of a second was employed.

## Chemicals

Benzophenone

Eastman's reagent was distilled under vacuum twice. At one mm pressure the ketone distilled at 120°C. The middle fraction of the second distillation was collected for further use and gave a melting point of 48.2° - 49.0°C. The benzophenone was stored in the inert atmosphere box and shielded from light.

Trimethylaluminum

Trimethylaluminum was obtained from Texas Alkyls Incorporated. The Batch Analytical Report received with this chemical showed trimethylaluminum was present to the extent of one-tenth of one percent. No other impurities were reported.

Since trimethylaluminum is prepared via methylaluminum halides (generally the trimethylaluminum sequenchloride) an analysis for halide content was made which gave a negative result.

Trimethylaluminum was further purified by distillation through a one foot packed column. Due to the high activity of this compound the distillation was carried out in the inert atmosphere box. The clear water

white liquid was stored in a 500 ml round bottom flask. The storage flask was fitted with a special joint containing a two mm bore teflon stopcock. The trimethylaluminum was stored in the dry box and samples were withdrawn by syringe via the teflon stopcock thereby avoiding impurities.

1,1-Diphenylethanol

Eastman's reagent was used without further purification.

Diethyl Ether

Baker's reagent (anhydrous) was distilled from lithium aluminum hydride prior to use.

Benzene

Fisher Certified thiophene free benzene was distilled from sodium aluminum hydride prior to use.

Magnesium Sulfate

Mallinckrodt Analytical Reagent Grade.

Calcium Chloride

Fisher Certified.

## Reaction of Trimethylaluminum with Benzophenone in Diethyl Ether

### Reaction Time and Product Analysis

Three 200 ml round bottom flasks were fitted with three-way glass stopcocks. Each flask was flamed and evacuated twice to 0.1 mm pressure and refilled with dry nitrogen. A nitrogen line was attached to each flask via the three-way stopcock in such a fashion that each flask could be kept under slight positive nitrogen pressure at all times.

A solution of 14.555g (.0799 moles) of benzophenone in 200 ml of ether (.3995M) was prepared in the dry box. A solution of trimethylalumi-

num (.1096 moles) in 200 ml of ether was also prepared. Septum caps were placed on both solutions and the solutions were removed from the dry box. To each of the first and second round bottom flasks 50 ml of trimethylaluminum solution was added, and 25 ml of trimethylaluminum solution was added to the third. Then 25 ml of benzophenone solution was added to the first flask and 50 ml was added to each of the other flasks. The addition of benzophenone was made as rapidly as possible with a 50 ml syringe. Upon addition of the ketone a yellow color developed immediately. The reaction flasks remained cool to the touch and no ether reflux was noted. The flasks were labeled and wrapped with aluminum foil to shield them from light.

Samples were withdrawn from the reaction flasks at periods of one, two, and four weeks. The samples were hydrolyzed with ten percent hydrochloric acid. The ether layer was drained off and dried over anhydrous $MgSO_4$. The samples were then analyzed by gas chromatography. The only product was 1,1-diphenylethanol. The areas under the gas chromatographic curves were determined by use of a planimeter. By use of standard samples it was determined that the ratio of the areas under the curves represent the ratio of mole percent of benzophenone and 1,1-diphenylethanol. The results are shown in Table 1.

The Ultraviolet Spectrum of Benzophenone in Ether

There are two major peaks in the ultraviolet spectrum. The peak representing the $\overline{\pi} \rightarrow \overline{\pi}^*$ transition occurs at 248.5 mμ. The extinction coefficient of this peak is difficult to determine precisely due to its magnitude. The determination requires weighing out very small quantities of benzophenone and diluting to very large volumes. The best value ob-

Table 1. Product from the Reaction of Trimethylaluminum with Benzophenone in Diethyl Ether

| $(CH_3)_3Al:(C_6H_5)_2CO$ | Reaction Time (weeks) | Percent 1,1-Diphenylethanol | Percent Benzophenone |
|---|---|---|---|
| 2.7:1 | 1 | 41.0 | 59.0 |
| 2.7:1 | 2 | 55.8 | 44.2 |
| 2.7:1 | 4 | 80.5 | 19.5 |
| 1.37:1 | 1 | 40.6 | 59.4 |
| 1.37:1 | 2 | 52.5 | 47.6 |
| 1.37:1 | 4 | 75.0 | 25.1 |
| .686:1 | 1 | 24.3 | 74.8 |
| .686:1 | 2 | 30.6 | 69.9 |
| .686:1 | 4 | 41.6 | 58.2 |

tained for the extinction coefficient was $1.76 \pm 0.2 \times 10^4$. Beer's Law was obeyed in concentration ranges from $2.00 \times 10^{-5}$M to $8.05 \times 10^{-5}$M.

The maximum representing the $n \rightarrow \overline{\pi}^*$ transition occurs at 344.5 mμ with an extinction coefficient of 119. In contrast Becker[20] reports extinction coefficients in tetrahydrofuran as follows: at 251 mμ, $\epsilon = 1.82 \times 10^4$, and at 343.5 mμ, $\epsilon = 128$. Duke[21] reports that at 251 mμ the extinction coefficient in ether is $1.84 \times 10^4$.

A trough occurs at 300 mμ. Benzophenone does not absorb at wavelengths longer than 400 mμ.

The Ultraviolet Spectrum of 1,1-Diphenylethanol

1,1-Diphenylethanol showed no absorbance at wavelengths longer than 300 mμ.

The Ultraviolet Spectrum of Trimethylaluminum

A 0.4352 M solution of trimethylaluminum in ether showed no absorbance at wavelengths longer than 241 mμ.

The Ultraviolet Spectrum of Trimethylaluminum-Benzophenone Mixtures

The general procedure for obtaining ultraviolet spectra was as follows. Two matched quartz cells were placed in the dry box entry port along with two 2 ml syringes. The entry port was then evacuated and refilled with dry nitrogen. The cells were filled in the dry box using 1.5 ml of standard ketone solution and 1.5 ml of standard trimethylaluminum solution. Standard benzophenone spectra were made by using 1.5 ml of pure diethyl ether in place of standard trimethylaluminum solution for comparison purposes. The cells were tightly stoppered with ground glass stoppers and then removed from the dry box for ultraviolet analysis.

A mixture of 1.5 ml of $6.19 \times 10^{-3}$ M benzophenone and 1.5 ml of

0.1 M trimethylaluminum gave an ultraviolet spectrum similar to that of benzophenone. A slight absorbance was noted in the 400 mμ to 500 mμ region. The ketone maximum at 344.5 mμ was somewhat flattened and the trough at 300 mμ was not quite so deep. When the concentration of trimethylaluminum was increased to 0.548 M, the absorbance in the 400 mμ to 500 mμ region increased. The trough at 300 mμ disappeared completely and a strong absorbance was found there. In addition the benzophenone maximum at 344.5 mμ appeared as a shoulder rather than as a peak.

In constrast to the 344.5 mμ benzophenone maximum, the benzophenone maximum at 248.5 mμ does not appear to be affected by large excesses of trimethylaluminum. When 1.5 ml of $10^{-4}$ benzophenone and 1.5 ml of pure diethyl ether are added to the quartz cell, the absorbance at 248.5 mμ was 1.05. When 1.5 ml of 0.4352 M trimethylaluminum is substituted for the pure ether the absorbance at 248.5 mμ does not change and the characteristic benzophenone spectra is maintained.

In a further experiment 1.5 ml of 0.4352 M trimethylaluminum was mixed with 1.5 ml of $10^{-4}$ M benzophenone in tightly stoppered ultraviolet cells. The ultraviolet spectrum between 350 mμ and 200 mμ was scanned every twenty-four hours. The cells were stored in the inert atmosphere box when spectra were not being recorded. The characteristic spectrum of benzophenone did not change with time except that it gradually decreased. A log absorbance plot showed that this decrease was first order with respect to the ketone with a half life of 112 hours.

Analysis

Benzophenone concentrations were determined by weighing out an appropriate amount and diluting this to the mark in a volumetric flask.

Aluminum concentration was determined by reaction with excess standard EDTA and then back titration with standard zinc acetate using dithizone as an indicator.

Reaction of Benzophenone with Trimethylaluminum in Benzene

Product Analysis and Extent of Reaction

Standard samples of benzophenone and 1,1-diphenylethanol in benzene were run on the gas chromatograph using matched two-foot carbowax 20-M columns. In all cases a pyrolysis product appeared. When the area under the curve of the pyrolysis product was added to the area under the alcohol curve the sum of the combined areas divided by the sum of the areas for 1,1-diphenylethanol, benzophenone, and the pyrolysis product gave the correct mole percent of 1,1-diphenylethanol.

A standard solution of benzophenone was prepared by dissolving 2.6558g of the ketone in 100 ml of benzene (0.1459 M) and stored in the dry box. A standard solution (0.1459 M) of trimethylaluminum in benzene was also prepared.

A 50 ml round bottom flask, a reflux condenser, and a three-way glass stopcock were flamed and placed in the dry box entry port. Also flamed and placed in the entry port were two 10 ml pipets. The port was evacuated twice to 0.5 mm pressure and refilled with nitrogen. The apparatus was moved into the dry box and 10 ml of 0.1459 M benzophenone solution and 10 ml of 0.1459 M trimethylaluminum solution were pipeted into the round bottom flask. The reflux condenser was attached to the flask and the three-way stopcock attached above the reflux condenser and closed off. The apparatus was held together tightly with rubber bands and held upright

with a ring stand and clamp. The apparatus was removed from the dry box and placed in a heating mantle. The three-way stopcock was attached to a nitrogen line and opened. The reaction mixture was allowed to reflux for twenty-four hours.

The reaction mixture was hydrolyzed with 50 percent hydrochloric acid. Samples were withdrawn from the hydrocarbon layer for analysis by gas chromatography using a matched set of two-foot Carbowax 20-M columns. The areas under the curves were measured with a planimeter. The product contained 96.5 percent, 1,1-diphenylethanol and 3.8 percent benzophenone.

In a similar experiment 10 ml of 0.1459 M trimethylaluminum was pipeted into the 50 ml flask containing 5 ml of 0.1459 M benzophenone. The mixture was allowed to reflux for two hours and the reaction period contained only 1,1-diphenylethanol.

In a further experiment 5 ml of 0.1459 M trimethylaluminum was added to 10 ml of 0.1459 M benzophenone. The reaction mixture was refluxed for eight days. Gas chromatographic analysis showed the product contained 48 percent 1,1-diphenylethanol and 52.2 percent benzophenone. This showed that only one methyl group from trimethylaluminum is available for reaction.

### Reaction of Trimethylaluminum with Benzophenone in Benzene in the Presence of Product

A standard solution of benzophenone was prepared by dissolving 2.655g of the ketone in 100 ml of benzene (0.1295 M) and stored in the dry box. A standard solution of trimethylaluminum in benzene (0.1291 M) was also prepared and stored in the dry box.

Reaction of $2(CH_3)_3Al$ with $(C_6H_5)_2CO$ in the Presence of $CH_3(C_6H_5)_2COAl(CH_3)_2$

Fifteen ml of a 0.1291 M solution of trimethylaluminum in benzene was pipeted into a 50 ml round bottom flask. Then five ml of 0.1295 M benzophenone was pipeted into the flask. The yellow color which developed initially disappeared in about 60 seconds. The flask was tightly stoppered and allowed to stand overnight to insure complete reaction. Then five ml of 0.1295 M benzophenone solution was added. The mixture was allowed to react for one hour, accurately timed, and hydrolyzed. Analysis by gas chromatography showed that 30 percent of the ketone had reacted.

Reaction of $(CH_3)_3Al$ with $(C_6H_5)_2CO$

Five ml of 0.1291 M trimethylaluminum solution was pipeted into a 50 ml round bottom flask containing 15 ml of benzene. The five ml of 0.1295 M benzophenone solution was added. The reaction was hydrolyzed after one hour and analysis by gas chromatography showed that 30.3 percent of the ketone had reacted.

Reaction of $2(CH_3)_3Al$ with $(C_6H_5)_2CO$

Ten ml of 0.1291 M trimethylaluminum solution was pipeted into a 50 ml round bottom flask containing ten ml of benzene. Then five ml of 0.1295 M benzophenone solution was added. The mixture was allowed to react for exactly one hour and hydrolyzed. Analysis by gas chromatography showed that 95.8 percent of the ketone had reacted.

The Ultraviolet Spectrum of Benzophenone

In benzene solution only one peak of benzophenone can be observed in the ultraviolet spectrum. The maximum occurs at 345 mμ with an extinction coefficient of 127 ± 2. The maximum obeys Beer's Law over the range

of concentrations from $7.6 \times 10^{-4}$ M to $1.60 \times 10^{-2}$ M. At wavelengths shorter than 270 mμ benzene itself absorbs so strongly that spectra cannot be obtained. Benzophenone does not absorb at wavelengths longer than 400 mμ.

The Ultraviolet Spectrum of 1,1-Diphenylethanol

1,1-diphenylethanol does not absorb over the entire range where spectra may be taken in benzene.

The Ultraviolet Spectrum of Trimethylaluminum

Trimethylaluminum does not absorb over the entire range where spectra may be taken in benzene.

Mixtures of Trimethylaluminum and Benzophenone

Spectra of mixtures of trimethylaluminum and benzophenone were obtained in the following fashion. A standard concentrated solution of benzophenone was prepared and stored in the inert atmosphere box. A matched set of quartz cells along with two tight fitting septum caps, a 50 μl syringe, a five ml syringe and pure distilled benzene were taken into the dry box. The matched quartz cells were filled with three ml of benzene, accurately delivered. The cells were sealed with septum caps and placed in the Cary 14 spectrophotometer. Then some standard benzophenone solution was removed from the box in the 50 μl syringe and a certain amount of this was injected through the septum cap into the sample quartz cell. The ultraviolet spectra of benzophenone was then recorded from 500 mμ to 300 mμ and the absorbance at 345 mμ was noted. This procedure was repeated several times and the average absorbance at 345 mμ was used to determine the concentration of benzophenone by means of the Beer's Law formula:

$$C = \frac{\text{abs.}}{127 \times 1}$$

C = molar concentration of benzophenone
Abs. = absorbance of benzophenone at 345 mμ
1 = cell path length in centemeters
127 = molar extinction coefficient of benzophenone at 345 mμ

The concentration of benzophenone in these experiments did not vary by more than ± 0.5 percent. Once the concentration of benzophenone was determined, appropriate standard solutions of trimethylaluminum could be prepared. Spectra of mixtures were then obtained in the manner described previously except that the standard trimethylaluminum solution was added to the sample cell rather than pure benzene.

When trimethylaluminum and benzophenone are added together in an ultraviolet cell in a 1:1 stoichiometry, the ketone spectra completely disappears. A strong new band appears in the 400 mμ to 500 mμ region. This band gradually disappears.

In one experiment 13 μl of standard benzophenone solution was added to 3.0 ml of trimethylaluminum solution in the quartz cell bringing the initial concentration of each component to 0.00911 M. The spectrum was scanned from 500 mμ to shorter wavelengths. The solution immediately turned yellow and the absorbance exceeded the limit of the instrument (2.0) at 400 mμ. The new band formed by the mixture between 400 mμ and 500 mμ gradually disappeared until after twenty hours the yellow color had disappeared and the absorbance was zero at 400 mμ. A strong absorbance was still found in the 400 mμ to 300 mμ region after twenty hours. After forty-eight hours the strong absorbance had completely disappeared and the

benzophenone spectrum reappeared with about 40 percent of its original strength.

When attempts were made to look at the spectrum of benzophenone with excess trimethylaluminum the new band disappeared so rapidly that the results were meaningless.

## Kinetic Experiments

### Kinetic Methods

Various physical methods have been employed in following the course of chemical reactions. The method most often used in following the kinetics of compounds containing chromophores is visible or ultraviolet spectroscopy. In the case where the reactant contains the chromophore, the disappearance of the absorption band can be followed. In the case where the product contains the chromophore the appearance of the new band can be followed. Often a reaction will go through a complex with a distinctive absorption band. In these cases the reaction of the complex can be observed directly.

### Techniques

There are several techniques for following reactions by visible and ultraviolet spectra. In the case of organometallic reactions with ketones the disappearance of the carbonyl chromophore can often be observed directly in the cell if the organometallic compound does not absorb near the ketone maximum.

In the cases where the organometallic compound absorbs in the region of the ketone the organometallic compound must be destroyed by quenching the reaction mixture before measurements can be made. This is also

true if a complex is formed which masks the carbonyl chromophore.

There are two methods employed in quenching reaction mixtures. If the reaction is slow the usual method employed is to set up a large reaction vessel and withdraw smaller samples for quenching at various times. If the reaction is very fast then separate smaller reactions are generally set up and quenched individually. The withdrawal method is preferred where it can be used. When individual quenching is employed extreme care must be taken to add the exact amount of each chemical. In addition each reaction flask must be treated in exactly the same way.

In the reaction of benzophenone with trimethylaluminum in benzene all three kinetic methods were employed. When benzophenone is mixed with trimethylaluminum a new band appears in the 400 mμ to 500 mμ region where neither the ketone nor the aluminum alkyl absorb. At an appropriate wavelength the disappearance of this band can be followed directly in the quartz ultraviolet cell. The new absorption band formed when trimethylaluminum is mixed with benzophenone masks the ketone maximum at 345 mμ. The species responsible for this new band must therefore be destroyed by quenching before the disappearance of the carbonyl chromophore can be observed. When trimethylaluminum and benzophenone are allowed to react in a 1:1 stoichiometry the reaction is slow enough to follow using the withdrawal technique. When excess trimethylaluminum is allowed to react with benzophenone, however, the reaction is so fast that sampling can be accomplished only by setting up individual reaction mixtures and quenching them at the appropriate time.

Essentially three kinetic techniques were employed to study the reaction of benzophenone with trimethylaluminum. Each will be discussed

fully.

## The Kinetics of the Complex Band

When trimethylaluminum and benzophenone are mixed a new band appears in the 400 mμ to 500 mμ region of the spectra. This band is quite intense in the 400 mμ region and much weaker near 500 mμ. The wavelength chosen for kinetic studies was 412 mμ. At this wavelength neither trimethylaluminum nor benzophenone absorb, and the intensity of the band is great enough to make accurate measurements with the spectrophotometer.

Twelve runs were made following the disappearance of the complex band with the ratio of reactants being 1:1. Two runs were made in which the ratio of trimethylaluminum to benzophenone was 2:1. In the runs in which trimethylaluminum was in excess, the data were not too reliable due to the swiftness of the reaction. Details can be found in the Appendix.

## Preparation of Reagents

A concentrated solution of benzophenone in benzene was prepared and stored in the dry box in a tinted flask.

A standard solution of approximately 0.1 M trimethylaluminum solution was prepared and stored in the dry box. This solution remained crystal clear for weeks. Kinetic solutions were prepared by dilution of a small amount of this standard solution in a 50 ml volumetric flask. Kinetic solutions were always used within twenty-four hours of their preparation.

## Preparation of the Quartz Cells and Addition of Reagents

A matched set of quartz cells were fitted with septum caps. The septum caps were extracted twice with benzene for three-day periods. The

septum caps fitted tight enough to cause a slight vacuum on the cells when they were removed.

The general procedure used was the following. The quartz cells, the septum caps, two five ml syringes and a 50 µl syringe were placed in the dry box entry port. The port was evacuated twice to 0.25 mm pressure and refilled with nitrogen. The equipment was then brought into the dry box. The reference cell was filled with three ml of freshly distilled benzene. The sample cell was filled with three ml of freshly prepared trimethylaluminum solution. The solutions were accurately delivered to the cells. The cells were then tightly fitted with septum caps. The 50 µl syringe was then filled to about 40 µl with a standard benzophenone solution and the cells, together with the 50 µl syringe were placed in the entry port. The cells were removed from the entry port and placed in the cell chamber of the Zeiss PMQ II spectrophotometer. The cell chamber was maintained at 25 ± 0.1°C.

After a suitable amount of time was allowed for the cells to come to temperature equilibrium, the cell chamber was opened briefly and an appropriate amount of benzophenone (i.e., six to 13 µl) was injected into the sample cell. The sample cell was quickly removed from the cell chamber and rolled once to insure proper mixing of the reactants and the cell was placed back in the chamber. The instrument was maintained in such a fashion that a reading could be taken immediately. The total time between the initial injection and the first reading was five to ten seconds. The first reading was taken to be the absorbance of the complex at zero reaction time.

Analysis

The concentration of benzophenone after delivery to the quartz cell was determined by Beer's Law, as previously described in this thesis.

The concentration of trimethylaluminum was determined in two ways. The first method was to determine the concentration of dilution from a previously prepared standard sample. The second method was to make a direct analysis for aluminum.

The concentration of aluminum alkyl used in these experiments was such that in order to get a meaningful analysis a large amount of solution had to be used. The method used was the following. A 50 ml volumetric flask was cleaned, flamed, cooled, and weighed along with its stopper. Then the flask was reflamed, wrapped in aluminum foil, and taken into a dry box. A solution for kinetic studies was prepared by dilution of a small amount of standard trimethylaluminum solution to 50 ml. After the amount of solution needed for kinetic studies had been withdrawn, the stoppered flask was removed from the dry box and reweighed. From the density of benzene at room temperature (i.e., 0.879 g/ml) and the weight of the trimethylaluminum solution, the volume of the trimethylaluminum solution was determined.

The contents of the flask was then hydrolyzed with ten percent hydrochloric acid. The benzene was evaporated with a heating mantel. An excess of approximately 0.01 M EDTA was added to the mixture and the mixture was then back-titrated with approximately 0.01 M zinc acetate using dithizone as an indicator.

The concentration of trimethylaluminum found by analysis always agreed quite well with that found by dilution.

## Reaction of Benzophenone with Trimethylaluminum in a 1:1 Ratio of Reactants: The Disappearance of the Carbonyl Absorption Band at 345 mμ

### Preparation of Reagents

A standard concentrated solution of benzophenone in benzene was prepared and stored in the inert atmosphere box in a tinted flask.

A standard solution of trimethylaluminum in benzene (approximately 0.1 M) was prepared and stored in the dry box. Solutions for kinetic studies were prepared by dilution of appropriate amounts of the standard solution in a 200 ml volumetric flask.

### Reaction Flask

A 100 ml round bottom flask with a 24/40 ground glass female joint was fitted with a 24/40 ground glass male joint attached to a three-way teflon stopcock. The stopcock was designed so that a strong flow of nitrogen could be maintained on the system when adding reagents or withdrawing samples. The details of the reaction flask are shown in Figure 1 below.

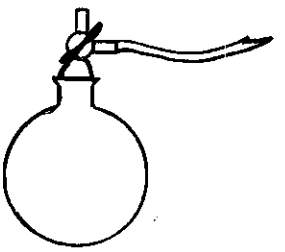


Figure 1. Kinetic Reaction Flask for Sample Withdrawl Technique

### Initiating, Timing, and Quenching of the Reaction

The reaction flask, along with a 100 ml volumetric flask and a two ml syringe were flamed and placed in the dry box entry port. The

entry port was evacuated twice to 0.25 mm pressure and refilled with nitrogen. The 100 ml volumetric flask was filled to the mark with standard trimethylaluminum solution and this was transferred to the reaction flask. Then the 24/40 male joint was attached to the reaction flask and the teflon stopcock was closed thereby sealing the system. The two ml syringe was filled with standard ketone solution and the reaction flask was removed from the box. The flask was placed in a constant temperature bath which maintained the temperature at 25 ± 0.2°C. A nitrogen line was attached to the flask in the position shown in Figure 1. After sufficient time had been allowed for the reaction flask and its contents to reach temperature equilibrium with the bath, the nitrogen valve to the stopcock was turned on and the stopcock was opened. An appropriate amount of standard benzophenone solution was added to the reaction flask via the two ml syringe. The flask was shaken lightly to insure mixing of the reactants and the timer was hit. An eight ml sample was withdrawn immediately and quenched in a test tube containing ten ml of ten percent hydrochloric acid. The test tube containing the quenched sample was labeled and the quenching of the first sample was about 50 seconds. After the first sample had been quenched the teflon stopcock was closed off thereby resealing the system and the nitrogen flow was cut off. Other samples were quenched in the same manner at appropriate times. The time necessary to withdraw a sample and quench it was about 20 seconds. The actual quenching required about three seconds and during this time the timer was read to the nearest second. It will be noted that a time error of three seconds is very small for reactions with half lives of 15,000 to 20,000 seconds.

Drying the Samples

One of the greatest frustrations of quenching benzene solutions is the fact that benzene forms an emulsion with water. Benzene samples which are quenched vigorously become cloudy. Samples which are quenched very lightly appear clear to the unaided eye but are quite opaque to ultraviolet light at 345 mμ.

Several methods were tried in an effort to clear up quenched solutions of benzophenone in benzene. If the quenched samples were allowed to sit overnight the benzene layer became clear to the unaided eye but still showed considerable absorbance at 345 mμ. This absorbance varied from sample to sample. If the organic layer was removed and placed over reagent grade calcium chloride the benzene layer immediately cleared up. Unfortunately, attempts to remove the organic layer were frustrated by small particles of calcium chloride suspended in the benzene layer. When anhydrous magnesium sulfate was used this problem was reduced considerably. Samples dried over magnesium sulfate, if handled carefully, remained crystal clear. In addition, extraneous absorption at 345 mμ due to water was completely eliminated. Benzophenone solutions which were quenched and dried over magnesium sulfate had the same absorbance as like samples which were unquenched.

The procedure followed in the kinetic studies is the following. After samples were quenched they were allowed to stand for one-half hour. This was time enough for large bubbles of hydrochloric acid solution to leave the benzene layer. A small layer of anhydrous magnesium sulfate was placed in a test tube. The test tube was then heated with a Fisher burner to remove the last traces of water from the magnesium sulfate. The

test tube was capped with a rubber stopper, which had been wrapped with aluminum foil, and allowed to cool. When the test tube had reached room temperature the benzene layer was removed from the quenched sample by syringe and injected into the test tube containing anhydrous magnesium sulfate.

Ultraviolet Analysis

The reference cell contained a sample trimethylaluminum solution which had been quenched and dried over anhydrous magnesium sulfate. The sample cell contained, of course, the quenched and dried reaction mixture. The best method for removing the samples from the test tubes containing the magnesium sulfate into the ultraviolet cells was simply to decant it.

After each reading was taken the sample cell was rinsed twice with acetone and twice with reagent grade anhydrous diethyl ether and dried under a flush of nitrogen. In between runs the quartz cells were stored under a layer of kerosene and were submerged for two hours in 50 percent hydrochloric acid prior to use.

Analysis of Reactants

Trimethylaluminum solutions were prepared for kinetic studies by dilution from standard approximately 0.1 M solutions. Aliquots of the kinetic solution were hydrolyzed with ten percent hydrochloric acid and the benzene layer was evaporated. Excess 0.01 M EDTA was added and the solution was titrated with standard 0.01 M zinc acetate using dithizone as an indicator. The analyzed results always agreed closely with those calculated from dilution.

In order to calculate the initial amount of benzophenone, additions of appropriate amounts of benzophenone were made to 100 ml of pure benzene

in the exact fashion used in kinetic runs. This was repeated several times and the concentration of benzophenone was calculated from Beer's Law using the average absorbance. The value of the absorbance of the first quenched sample was always close to the average value of the absorbance found by the method just described. The value for the absorbance of the first quenched sample in a kinetic run was therefore taken as the absorbance of benzophenone at zero reaction time.

It should be noted that in the kinetic method employed samples were never diluted. This eliminated errors resulting from the exact size of sample withdrawal or from dilution factors. It should also be noted that neither benzophenone solutions or trimethylaluminum solutions were exposed to the atmosphere prior to quenching.

## Reaction of Benzophenone with Excess Trimethylaluminum: The Disappearance of the Carbonyl Absorption Band at 345 mμ

The experimental procedure followed during the course of this study was modeled after that of Anteunis[22] and developed further by Duke[21]. The experimental details are somewhat different as will be discussed later.

### Preparation of Reagents

A standard concentrated solution of benzophenone in benzene was prepared and stored in the dry box in a tinted flask.

A standard solution of trimethylaluminum in benzene (about 0.1 M) was prepared and stored in the dry box. Solutions for kinetic studies were prepared by dilution of appropriate amounts of the standard solution in a 200 ml volumetric flask.

### Reaction Flasks

Special reaction flasks were employed in the kinetic studies of

benzophenone with excess trimethylaluminum due to the speed of the reaction. These were 25 ml glass stoppered volumetric flasks with a glass sidearm between the stopper and the graduation mark. The sidearm was about 20 mm in length and 10 mm in diameter. It was tilted downward so that it formed an angle of about 60 degrees with the neck of the flask. The glass stoppers had small glass hooks protruding from one side which allowed the stoppers to be held securely in the flask by rubber bands extending between the hooks and the sidearms of the reaction flasks.

Addition of Reagents

A wooden stand with clamps was placed in the dry box entry port along with a 50 μl syringe. The kinetic flasks, the glass stoppers, and a 10 ml syringe were flamed and placed in the entry port while hot. The entry port was sealed and evacuated twice to 0.25 mm pressure and refilled with nitrogen. The wooden stand was removed to the dry box and the kinetic flasks were clamped into place. An appropriate amount of benzophenone solution (15, 20, or 30 μl) was added to the sidearm of the flask using the 50 μl syringe. An eight ml aliquot of standard trimethylaluminum solution was then transferred by syringe to the lower portion of each reaction flask taking care to prevent the organoaluminum compound from getting into the sidearm containing the benzophenone. The ground glass stoppers were then securely seated in the necks of the flasks and fastened in place with rubber bands. After the transfers were complete the reaction flasks were removed from the inert atmosphere box.

Initiating, Timing, and Quenching of the Reactions

All but two of the reaction flasks were placed in a constant temperature bath at 25 ± .02°C. Just the lower bulbs of the flasks were

immersed leaving the necks and the ground glass stoppers above water in order to carry out subsequent operations. The contents of the two remaining reactions flasks, one of which did not contain benzophenone, were hydrolyzed with ten percent hydrochloric acid. The sample containing the benzophenone served as a measure of the initial ketone concentration at zero time and the other was employed in the reference ultraviolet cell to compensate for the absorbance of the solvent.

After adequate time had elapsed for the reactants to come to thermal equilibrium, a reaction was initiated by repeated inversions of the flask. The electric stopclock was started at the same time the reactants were mixed. The reactions were quenched by adding ten ml of a ten percent solution of hydrochloric acid from a syringe. The stopclock was stopped at the moment the syringe plunger was depressed. The entire operation of opening the reaction flask, quenching the reaction mixture, and stopping the stopclock could be accomplished in about a second. Since the yellow color characteristic of the trimethylaluminum-benzophenone complex disappeared with the first small amount of hydrochloric acid solution, the reactions were probably effectively quenched in about 0.2 seconds.

Drying the Samples

The flasks were labeled and set aside. The benzene layer was removed and dried over anhydrous magnesium sulfate in a manner previously described to remove water from the benzene layer.

Ultraviolet Analysis

The samples were carefully decanted from the test tubes containing magnesium sulfate into quartz ultraviolet cells. Ultraviolet readings of the benzophenone maximum at 345 mμ were made in a manner previously de-

scribed.

Analysis of Reactants

In order to determine the concentration of benzophenone at zero reaction time the kinetic flasks were taken into the dry box. Additions of standard benzophenone solution and standard trimethylaluminum solution were made in the exact manner as for a kinetic run. Without first initiating the reaction, each sample was quenched with ten percent hydrochloric acid. The hydrolyzed benzene layer was then mixed with the benzophenone solution in the sidearm. The samples were dried over anhydrous magnesium sulfate and ultraviolet readings were made. From the average absorbance of these samples the concentration of benzophenone at zero reaction time was calculated from Beer's Law. When an actual kinetic run was made one reaction flask was hydrolyzed prior to the mixing of the reactants. If the value of the concentration of benzophenone in this flask varied by more than one percent from the average concentration of benzophenone at zero reaction time, the run was discarded. A difference of one percent could only occur if the solution in the reference cell had not been properly dried or if a gross error in addition had been made. Fortunately, this never occurred and no run was discarded for this reason.

Trimethylaluminum solutions were prepared for kinetic studies by dilution from standard solutions. Aliquots of the kinetic solution were hydrolyzed with ten percent hydrochloric acid and the benzene layer was evaporated. Excess 0.01 M EDTA was added and the mixture was back titrated with 0.01 M zinc acetate (exact concentrations varied slightly) using dithizone as an indicator. The analyzed results always agreed quite closely with those calculated from dilution.

It should be noted that in the kinetic method employed samples were never diluted and thus dilution errors were eliminated. Also, trimethylaluminum solutions and benzophenone solutions were never exposed to the atmosphere as the addition of both reagents was done in the dry box.

## Inert Atmosphere Box and Purification System

All transfers of trimethylaluminum and benzophenone solutions were made in an inert atmosphere box equipped with an evacuable entry port. Dry oil-pumped nitrogen was employed as the inert gas. A Gelman little giant recirculating pump, which was sealed from the atmosphere to prevent leakage moved the box atmosphere at a rate of about one cubic foot a minute.

### Purification System

The purification system employed in connection with the recirculating system was essentially that proposed by Brown[23]. The exit gases from the box were first passed through a duel trap at dry ice-acetone temperature. This removed most of the water and organic vapors. The gases were then pushed through a column of magnese (II) oxide to remove any oxygen in the atmosphere. From there the gases passed over a column of indicating Drier Rite and finally through a second duel trap at dry ice-acetone temperature. The atmosphere was pushed from the final dry ice trap to the dry box.

### Operation of the Inert Atmosphere Box

The recirculating system was kept running continuously except for a shut-down once a week to clean the dry ice traps. The last finger of

the second dry ice trap collected a negligible amount of refuse during the course of a week, indicating that trapping was effective. The MnO columns were regenerated as needed. The columns would generally be effective oxygen scrubbers for about three days when the dry box was properly maintained. A small dish of $P_2O_5$ was stored in the dry box to indicate the extent of contamination by moisture. On two days standing in the box the $P_2O_5$ developed the slightest layer of crust, which was removed as needed. Whenever possible the box was entered by placing the materials to be taken into the box in the entry port and evacuating the port to at least 0.5 mm pressure and refilling with nitrogen. When kinetics were being run all kinetic equipment was flamed and moved into the box only after evacuating twice to 0.25 mm pressure and refilling the entry port with nitrogen. When solvents or solutions had to be taken into the box they were placed in the entry port and the port was flushed with nitrogen for at least fifteen minutes. If flushing was done properly it was reasonably effective although not as effective as evacuation.

Proper use of the dry box is time consuming. The best atmosphere cannot be maintained without the complete cooperation of all parties using the dry box. Often weeks are required to bring the quality of the atmosphere in the dry box up to the proper level. The research results obtained through proper maintenance of a good inert atmosphere are well worth the effort.

# CHAPTER III

## DISCUSSION AND RESULTS

### Reaction of Benzophenone and Trimethylaluminum in Benzene

Benzophenone and trimethylaluminum were found to give the expected product without the side reactions of enolization and reduction. When the reactants are in a 1:1 ratio the yield of addition product, after prolonged reflux, is 96 percent. Furthermore, only one methyl group is available for methylation. When benzophenone and trimethylaluminum in a 2:1 ratio were allowed to reflux in benzene for eight days the final product after hydrolysis contained equal amounts of benzophenone and 1,1-diphenylethanol. This shows that the dimethylaluminum carbinolate is unreactive toward benzophenone. It also appears unlikely that equilibrium (1) leads to a significant concentration of trimethylaluminum.

$$2(CH_3)_2AlOC(C_6H_5)_2CH_3 \rightleftarrows (CH_3)_3Al + CH_3Al\left(OC(C_6H_5)_2CH_3\right)_2 \quad . \qquad (1)$$

When two parts trimethylaluminum were allowed to react with one part benzophenone the reaction was found to be nearly complete after one hour. When two parts trimethylaluminum were allowed to react with one part benzophenone in the presence of one part dimethylaluminum 1,1-diphenylmethylcarbinolate, the reaction was only 30 percent complete in one hour. When one part trimethylaluminum was allowed to react with one part benzophenone the reaction was 30 percent complete in one hour. This indicates that each molecule of dimethylaluminum-1,1-diphenylmethylcarbinolate ties up a

molecule of trimethylaluminum and makes it unavailable for reaction.

Ultraviolet Spectra

When equal amounts of trimethylaluminum and benzophenone are mixed in benzene the ultraviolet spectrum of the ketone completely disappears and a strong absorbance appears over the entire range from 270 mμ to 500 mμ. Ultraviolet spectral changes have been equated to complex formation when organometallic compounds are added to ketones. In view of the drastic changes in the benzophenone spectrum with the addition of trimethylaluminum, it appears that complexation is nearly complete. This is not unreasonable. Trimethylaluminum is a strong Lewis acid and benzophenone is a Lewis base. In a non-polar solvent the two would be expected to combine rather strongly. With the absence of other polar molecules to compete with benzophenone for trimethylaluminum, the equilibrium mixture should favor the complex. This finding is in agreement with ebulliometric data by Mole[16], that trimethylaluminum and benzophenone form a monomeric complex in benzene with no free ketone or organoaluminum compound remaining. Grignard reagents, by contrast, are reported not to complex completely to ketones. These are prepared in polar solvents which offer strong competition to the ketones for the organomagnesium compound.

## Kinetic Studies

The reaction of trimethylaluminum with benzophenone in benzene was studied by following the disappearance of the ketone carbonyl band at 345 mμ and by following the disappearance of the complex band at 412 mμ in a region where neither the ketone nor the aluminum alkyl absorb. The reaction was studied at trimethylaluminum to ketone ratios ranging from

.855:1 to 3.76:1. This was the widest range which the nature of the reaction would allow. In addition, the aluminum alkyl and ketone concentrations were varied over a range of several fold.

For the purpose of discussion, the reaction of trimethylaluminum with benzophenone where the ketone is equal to or in excess of the aluminum alkyl will be considered separately from the case where excess trimethylaluminum was used. This is due to the drastic changes which take place in the rate of the reaction when excess trimethylaluminum is used. The mathematical analyses of both cases contain some common assumptions. The first is that the equilibrium constant governing the formation of the complex is very large. The second assumption is that the stoichiometry of the complex that is formed is 1:1.

### Reaction of Trimethylaluminum with Benzophenone in Which the Ketone is Equal to or in Excess of the Organoaluminum Compound

When trimethylaluminum and benzophenone are allowed to react in a 1:1 stoichiometry the complex band at 412 mμ disappeared in a first-order fashion for 65 to 70 percent reaction. The first-order rate constants were calculated from equation (2):

$$k_{obs} = \frac{2.3}{t} \log \frac{A_o - A_\infty}{A - A_\infty} \quad , \qquad (2)$$

where A is the absorbance at time t, $A_o$ is the absorbance at zero reaction time, and $A_\infty$ is the absorbance at infinite reaction time. The data for individual runs are given in Tables 6 through 17 in the Appendix. The average rate constants for the disappearance of the complex band are shown in Table 2. The first three values shown were calculated from runs in

Table 2. Rate Constants for the Reaction of Trimethylaluminum with Benzophenone. Disappearance of the Complex Band at 25°C.

| $10^3(C_6H_5)_2CO$ M | $10^3(CH_3)_3Al$ M | $10^4 k_{obs}$ [c] $sec^{-1}$ |
|---|---|---|
| 6.58 | 6.60[a] | 2.44 ± 0.09 |
| 6.58 | 6.60[a] | 2.55 ± 0.03 |
| 6.58 | 6.60[a] | 2.49 ± 0.07 |
| 6.91 | 6.90[b] | 2.32 ± 0.05 |
| 6.91 | 6.90[b] | 2.35 ± 0.05 |
| 6.91 | 6.90[b] | 2.41 ± 0.04 |
| 9.11 | 8.90[b] | 2.33 ± 0.04 |
| 9.11 | 8.90[b] | 2.50 ± 0.04 |
| 9.11 | 8.90[b] | 2.43 ± 0.03 |
| 4.44 | 4.15[b] | 2.42 ± 0.03 |
| 4.44 | 4.15[b] | 2.41 ± 0.11 |
| 4.44 | 4.15[b] | 2.41 ± 0.12 |

[a] Concentration determined by dilution

[b] Concentration determined by direct analysis

[c] Calculated from Equation (2)

which the trimethylaluminum concentration was determined by dilution only. The remaining values were calculated from runs in which the trimethylaluminum concentration was determined by direct analysis. Little if any difference can be seen between the average rate constants in the two sets of runs.

The first-order behavior of the complex band continued through about two half lives. Figure 2 provides an example. Beyond two half lives serious deviation from first-order behavior occurred.

The kinetics of the reaction of trimethylaluminum with benzophenone in a reactant ratio 1:1 was also followed by observing the disappearance of the ketone maximum at 345 mμ. In order to observe this maximum it was necessary to quench the reaction in ten percent hydrochloric acid in order to destroy the complex which also absorbs strongly at 345 mμ. Thus, the experimental reading of the ketone concentration at 345 mμ after quenching actually represents the amount of uncomplexed ketone and unreacted complex in the unquenched reaction. The disappearance of the ketone maximum at 345 mμ was found to be more complex and much slower than the disappearance of the complex band at 412 mμ. Simple first-order behavior was not observed. A relationship between the behavior of the complex band and the behavior of the ketone maximum was noticed, however. When the complex band had reached 50 percent reaction the ketone maximum had reached approximately 25 percent reaction. In other words, the ketone maximum disappeared at about half the rate of the complex band. This suggested that a mechanism of the following type may be involved:

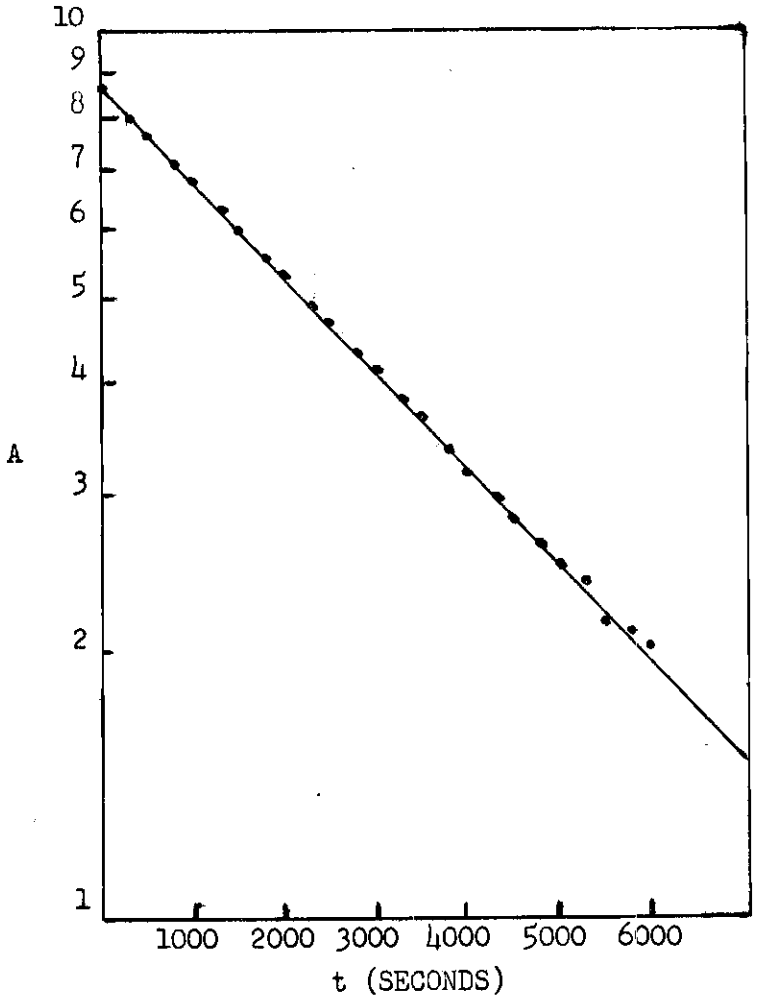



Figure 2. First-order Disappearance of Complex Band at 25°C. (Data from Table 16, in Appendix.)

$$A_2 \rightleftarrows 2A \quad \text{rapid}$$

$$A + K \rightleftarrows C \quad \text{rapid}$$

$$C \xrightarrow{k} P' \quad \text{rate controlling}$$

$$P' + A \rightarrow P \quad \text{rapid and complete} \qquad (3)$$

where $A_2$ represents the trimethylaluminum dimer; K represents the ketone, benzophenone; P′ represents the dimethylaluminum carbinolate formed from an internal transfer of a methyl group via the complex C, and P is the product formed from the reaction of P′ with a molecule of trimethylaluminum. It is assumed that the fourth step proceeds so rapidly and completely that P is the only product. Mechanism (3) would show the type of behavior found for the complex and ketone if the equilibrium constant for the second step is very large. If mechanism (3) is operative the disappearance of the complex would be given by equation (2), with $k_{obs} = 2k$. The differential equation expressing the disappearance of the ketone maximum according to mechanism (3) is given by equation (4):

$$\frac{dx}{dt} = -\frac{dP'}{dt} = -kC = -2k(x-\tfrac{1}{2}Ko) \quad , \qquad (4)$$

where x is the variable measured, K + C. The solution to equation (4) is given by equation (5):

$$k' = 2k = \frac{2.3}{t} \log \frac{x_o - K_o + \frac{1}{2}A_o}{x - K_o + \frac{1}{2}A_o} \quad , \qquad (5)$$

where K represents the amount of benzophenone at time t and $A_o$ is the analytically calculated amount of trimethylaluminum at zero reaction time.

A complete derivation of equation (5) can be found in the Appendix, Derivation 1. The data for individual runs are given in Tables 18 through 23 in the Appendix. The rate constants calculated from equation (5) are given in Table 3.

One test of the validity of the proposed mechanism is a comparison of $k_{obs}$ and $k'$, since each should be equal to 2k. The average value for $k_{obs}$, calculated from the disappearance of the complex band by use of equation (2) is $2.41 \times 10^{-4}$ $sec^{-1}$. The average value of $k'$, calculated from equation (5) for the disappearance of the benzophenone maximum is $1.80 \times 10^{-4}$ $sec^{-1}$. The agreement, while close, is not completely satisfactory. This suggests that the mechanism is nearly correct but requires some modification.

The incomplete nature of mechanism (3) is also apparent from the following considerations. Mechanism (3) demands that only one-half of the benzophenone react. Thus, in rate expression (5) the infinity value which must be subtracted from the concentration of benzophenone at time t is one-half the initial value of benzophenone. The fact that benzophenone reacts past 50 percent, although slowly, shows that this choice is incorrect.

It should also be pointed out that the spectrum generated by the complex when trimethylaluminum and benzophenone are reacted in a 1:1 ratio gradually disappears and regenerates the ketone spectrum. The absorbance of the ketone maximum after the complex disappears indicates that about 60 percent to 65 percent of the ketone has reacted. The benzophenone maximum then continues to disappear slowly. Some time after 50 percent of the ketone has reacted the amount of complex is so small that it no

Table 3. Rate Constants for the Reaction of Trimethylaluminum with Benzophenone. Disappearance of the Ketone Carbonyl Band at 25°C.

| $10^3(C_6H_5)_2CO$ M | $10^3(CH_3)_3Al$ M | $10^4k'$[a] $sec^{-1}$ |
|---|---|---|
| 8.15 | 8.08 | 1.78 ± 0.12 |
| 8.17 | 8.28 | 1.42 ± 0.09 |
| 8.35 | 8.28 | 1.51 ± 0.07 |
| 15.71 | 15.82 | 1.90 ± 0.07 |
| 16.05 | 16.00 | 2.08 ± 0.14 |
| 16.05 | 13.72 | 2.09 ± 0.08 |

[a] Calculated from Equation (5)

longer appears in the ultraviolet spectrum. When the ketone spectrum reappears about 40 percent of the trimethylaluminum is still unreacted. Since this trimethylaluminum is not complexed to the benzophenone it must be complexed to the dimethylaluminum carbinolate.

A mechanism which qualitatively takes into account the observations of the preceding paragraph is:

$$A \rightleftarrows 2A \quad \text{rapid}$$

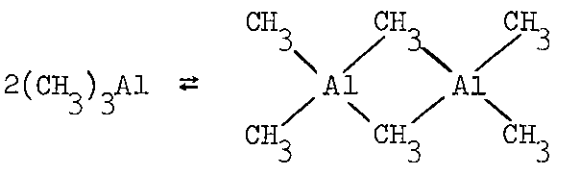
$$A + K \rightleftarrows C \quad \text{rapid}$$

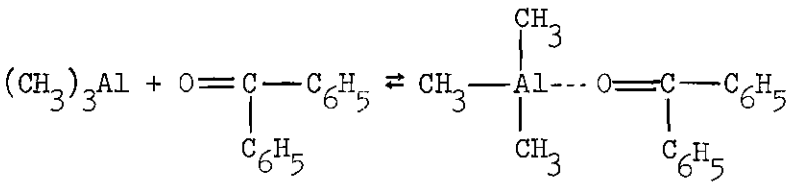
$$C \rightarrow P' \quad \text{rate controlling}$$

$$P' + A \rightleftarrows P \quad \text{rapid} \qquad (6)$$

where the symbols represent the same species as in mechanism (3). In mechanism (6) both P and P′ appear as products present in a measurable amount. Due to the difficulty in the mathematics, the data were not analyzed according to mechanism (6).

Thus, the following equations show the detailed mechanism by which trimethylaluminum is thought to react with benzophenone when the ketone is equal to or in excess of the aluminum alkyl.





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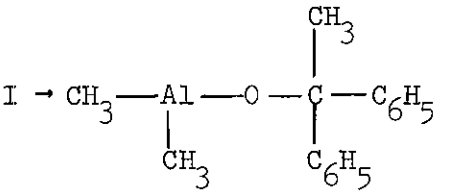
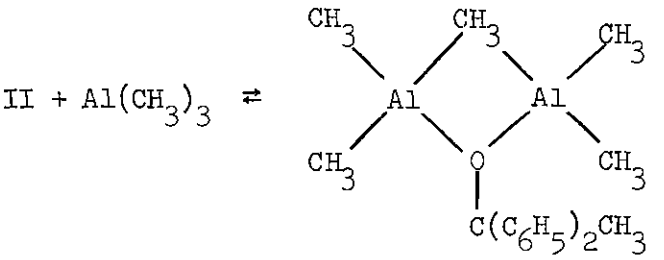


II



A strong case has been presented to show that trimethylaluminum and benzophenone react in a 1:1 stoichiometry according to mechanism (6). It is recognized, however, that a more detailed treatment of the data might give better results.

## Reaction of Benzophenone with Excess Trimethylaluminum

When benzophenone is allowed to react with excess trimethylaluminum a tremendous rate increase is found. A reaction mixture with an initial ketone concentration of $8.17 \times 10^{-3}$ M and an initial trimethylaluminum concentration of $8.28 \times 10^{-3}$ M $\left((CH_3)_3Al/(C_6H_5)_2CO = 1.01/1\right)$, has an experimental half life of about 20,000 seconds at 25°C. By contrast, a reaction mixture with an initial trimethylaluminum concentration of $15.15 \times 10^{-3}$ M and an initial ketone concentration of $7.55 \times 10^{-3}$ M

$\left((CH_3)_3Al/(C_6H_5)_2CO = 2/1\right)$ has an experimental half life of about 58 seconds at 25°C. When the ratio of trimethylaluminum to benzophenone is 1.5:1.0, the rate of the reaction is greatly enhanced until 50 percent of the benzophenone has reacted. After 50 percent of the ketone has reacted the reaction becomes very slow. This type of behavior excludes the possibility of simple first-, second-, or third-order kinetics. What it does suggest is that upon addition of reactants a complex is formed immediately, which then reacts with further trimethylaluminum to give product in a rate controlling step. The fact that when a fractional excess of trimethylaluminum is used the initial reaction rate is increased but not the rate throughout the reaction, shows that the product formed from the reaction of the complex with a further molecule of trimethylaluminum does not readily release trimethylaluminum.

It has already been pointed out that trimethylaluminum in benzene solvent consists of an equilibrium mixture of monomers and dimers with the equilibrium predominately favoring the dimer in the concentration range where association measurements have been made. The experimental data were analyzed in three ways. In the first method the aluminum alkyl was considered to be predominantly dimeric with the dimer reacting to give product. This method is referred to as the dimer-dimer analysis. In the second method the aluminum alkyl was considered to be predominantly dimeric with the monomer reacting with the complex to give product. This method is referred to as the dimer-monomer analysis. Due to certain trends in the data it was recognized that at very low aluminum alkyl concentrations the solution may contain a considerable proportion of trimethylaluminum monomer. Thus, in the last method of analysis the aluminum alkyl was con-

sidered to be predominantly monomeric with the monomer reacting with the complex to give product. This method is referred to as the monomer-monomer analysis. It should be noted that the designation for these methods of analysis are such that the predominant species is indicated first and the reactive species second.

The Dimer-Dimer Analyssis

The reaction of trimethylaluminum with benzophenone to give product by the trimethylaluminum dimer attacking the complex may be represented by mechanism (7):

$$A_2 \rightleftarrows 2A \qquad \text{rapid}$$

$$A + K \rightleftarrows C \qquad \text{rapid}$$

$$C + A_2 \xrightarrow{k_d} P + A \qquad \text{rate-determining} \qquad (7)$$

where $A_2$ is the trimethylaluminum dimer, A is the trimethylaluminum monomer, C is the complex formed between trimethylaluminum and the ketone K, and P is the reaction product. The assumptions are that the reaction between trimethylaluminum and benzophenone to form a complex is extremely rapid. The reaction of the complex with trimethylaluminum dimer to give the product is rate controlling. It will be noted that in this analysis the manner in which the complex comes into being is not important so long as its formation is immediate. Further assumptions are that the stoichiometry of the complex is one trimethylaluminum to one benzophenone, that the equilibrium governing formation of the complex is displaced so far to the right that no uncomplexed ketone exists, and the stoichiometry of

the product P is two trimethylaluminum to one benzophenone.

The differential equation expressing the disappearance of the complex is given by (8):

$$\frac{dC}{dt} = -\frac{k_d}{2} C(C+A-2K) \quad , \tag{8}$$

where C is the complex at time t, A is the analytically measured amount of trimethylaluminum, and K is the initial concentration of benzophenone. The solution to equation (8) is given by (9):

$$k_d = \frac{2.3 \times 2}{t(A-2K)} \log \frac{C_o(C+A-2K)}{C(C_o+A-2K)} \quad , \tag{9}$$

where $C_o$ is the amount of complex at zero reaction time. For the special case where A = 2K, the differential equation expressing the disappearance of complex is given by (10):

$$\frac{dC}{dt} = -\frac{k_d}{2} C^2 \quad . \tag{10}$$

The solution to equation (10) is given by (11):

$$k_d = \frac{2}{t}\left(\frac{1}{C} - \frac{1}{C_o}\right) . \tag{11}$$

Since the amount of ketone found upon quenching the samples is equal to the amount of complex at time t, according to the assumption made, calculations were straightforward. Complete derivations of equations (9) and (11) can be found in the Appendix, Derivation 2. The results of the calculations are shown in Table 4.

Table 4. Reaction of Trimethylaluminum with Benzophenone. Constants Calculated for the Dimer-Dimer Mechanism and Dimer-Monomer Mechanism.

| $10^3(C_6H_5)_2CO$ M | $10^3(CH_3)_3Al$ M | $\frac{(CH_3)_3Al}{(C_6H_5)_2CO}$ | $k_d$ l mole$^{-1}$ sec$^{-1}$ | $k\sqrt{K_D}$ l$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec$^{-1}$ |
|---|---|---|---|---|
| 11.30 | 17.41 | 1.54 | 5.00 ± 0.30[a] | .227 ± .024[c] |
| 7.55 | 12.64 | 1.68 | 4.90 ± 0.28[a] | .219 ± .013[c] |
| 7.55 | 13.21 | 1.75 | 5.18 ± 0.32[a] | .235 ± .017[c] |
| 7.55 | 15.15 | 2.00 | 4.82 ± 0.32[b] | .226 ± .018[d] |
| 7.55 | 15.34 | 2.03 | 4.10 ± 0.30[b] | .203 ± .020[d] |
| 11.30 | 22.86 | 2.02 | 4.12 ± 0.34[b] | .255 ± .006[d] |
| 5.68 | 11.70 | 2.06 | 4.48 ± 0.26[b] | .208 ± .019[e] |
| 11.30 | 25.28 | 2.21 | 4.32 ± 0.26[a] | .281 ± .019[e] |
| 7.55 | 18.93 | 2.50 | 3.72 ± 0.30[a] | .246 ± .007[e] |
| 5.68 | 16.26 | 2.93 | 3.54 ± 0.12[a] | .251 ± .008[e] |
| 7.55 | 22.97 | 3.04 | 3.44 ± 0.10[a] | .275 ± .008[e] |
| 5.68 | 21.38 | 3.76 | 3.24 ± 0.22[a] | .276 ± .016[e] |

[a] Calculated from Equation (9)

[b] Calculated from Equation (11)

[c] Calculated from Equation (15)

[d] Calculated from Equation (17)

[e] Calculated from Equation (14)

The Dimer-Monomer Analysis

The reaction of trimethylaluminum with benzophenone to give product via attack on the initial complex formed by monomeric trimethylaluminum is represented by mechanism (12):

$$\begin{aligned} A_2 &\overset{K_D}{\rightleftharpoons} 2A && \text{rapid} \\ A + K &\rightleftharpoons C && \text{rapid} \\ C + A &\overset{k}{\rightarrow} P && \text{rate-determining} \quad . \end{aligned} \tag{12}$$

The assumptions in analyzing the data according to mechanism (12) are the same as those made in analyzing the data according to mechanism (7) except that the rate controlling step involves the attack of monomeric trimethylaluminum on the complex to form the product. The rate constant k cannot be calculated directly for mechanism (12). The product of the rate constant and the square root of the dissociation constant for dimeric trimethylaluminum, $k\sqrt{K_D}$, can be calculated for mechanism (12). This constant can then be used for comparison purposes with rate constants calculated for mechanism (7).

The differential equation for the disappearance of complex according to mechanism (12) is given by (13):

$$\frac{dC}{dt} = -\frac{k\sqrt{K_D}}{\sqrt{2}} C(C+A-2K)^{\frac{1}{2}} \quad , \tag{13}$$

where $K_D$ is the dissociation constant of trimethylaluminum, $K_D = A^2/A$, and other symbols represent the same species as in mechanism (7). There

are two solutions for equation (13). When A is greater than 2K the solution is given by (14):

$$k\sqrt{K_D} = \frac{2.3\sqrt{2}}{t\sqrt{A-2K}}\log\frac{\left(\sqrt{C_o+A-2K} - \sqrt{A-2K}\right)\left(\sqrt{C+A-2K} + \sqrt{A-2K}\right)}{\left(\sqrt{C_o+A-2K} + \sqrt{A-2K}\right)\left(\sqrt{C+A-2K} - \sqrt{A-2K}\right)} . \quad (14)$$

When A is less than 2K the solution is given by (15):

$$k\sqrt{K_D} = \frac{2\sqrt{2}}{t\sqrt{2K-A}}\left(\tan^{-1}\sqrt{\frac{C_o+A-2K}{2K-A}} - \tan^{-1}\sqrt{\frac{C+A-2K}{2K-A}}\right) . \quad (15)$$

For the special case where A = 2K, the proper differential equation for the disappearance of the complex is given by (16):

$$\frac{dC}{dt} = -\frac{k\sqrt{K_D}}{\sqrt{2}}C^{3/2} . \quad (16)$$

The solution to equation (16) is given by (17):

$$k\sqrt{K_D} = \frac{2\sqrt{2}}{t}\left(\frac{1}{\sqrt{C}} - \frac{1}{\sqrt{C_o}}\right) . \quad (17)$$

Complete derivations of the equations governing the disappearance of the complex according to mechanism (12) are given in the Appendix, Derivation 3. The results are shown in Tables 4 and 5.

The Monomer-Monomer Analysis

A solution of trimethylaluminum in benzene may contain a considerable proportion of monomer at very low concentrations. Certain trends in the rate data indicated that at concentrations of trimethylaluminum less

Table 5. Reaction of Trimethylaluminum with Benzophenone. Constants Calculated for the Dimer-Monomer Mechanism and the Monomer-Monomer Mechanism.

| $10^3(C_6H_5)_2CO$ M | $10^3(CH_3)_3Al$ M | Free $(CH_3)_3Al$ M | k $l\ mole^{-1}\ sec^{-1}$ | $k\sqrt{K_D}$ $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ | $k\sqrt{K_D}$ [a] $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ |
|---|---|---|---|---|---|
| 7.55 | 12.64 | 5.09 | 2.45 ± 0.14[b] | .219 ± .013[d*] | .240 ± .010[d] |
| 7.55 | 13.21 | 5.66 | 2.59 ± 0.16[b] | .235 ± .017[d*] | .250 ± .009[d] |
| 7.55 | 15.34 | 5.79 | 2.05 ± 0.15[c] | .203 ± .020[f*] | .222 ± .014[f] |
| 5.68 | 11.70 | 6.02 | 2.24 ± 0.13[c] | .208 ± .019[e*] | .226 ± .010[e] |
| 11.30 | 17.41 | 6.11 | 2.50 ± 0.15[b**] | .227 ± .024[d*] | .247 ± .015[d] |
| 7.55 | 15.15 | 7.60 | 2.41 ± 0.16[c**] | .226 ± .018[f*] | .243 ± .011[f] |
| 5.68 | 16.26 | 10.58 | 1.77 ± 0.06[b**] | .251 ± .008[e] | |
| 11.30 | 22.86 | 11.56 | 2.06 ± 0.17[c*] | .255 ± .006[f] | |
| 7.55 | 18.93 | 12.38 | 1.86 ± 0.15[b*] | .246 ± .007[e] | |
| 11.30 | 25.28 | 13.98 | 2.16 ± 0.13[b*] | .281 ± .019[e] | |
| 7.55 | 22.97 | 15.42 | 1.72 ± 0.05[b*] | .275 ± .008[e] | |
| 5.68 | 21.38 | 15.70 | 1.62 ± 0.11[b*] | .276 ± .016[e] | |

[a] Averaged from values constituting 50 percent reaction or less
[b] Calculated from Equation (20)
[c] Calculated from Equation (22)
[d] Calculated from Equation (15)
[e] Calculated from Equation (14)
[f] Calculated from Equation (17)
* Drift in constants with reaction time during individual run
** Slight drift in constants with reaction time during individual run

than 0.005 M, a significant proportion of trimethylaluminum exist as monomer.

Mechanism (18) represents the reaction of trimethylaluminum with benzophenone to give product via attack on the initial complex formed by monomeric trimethylaluminum. It should be noted that mechanism (18) is the same as mechanism (12) except for the assumptions involved.

$$A_2 \rightleftarrows 2A \quad \text{rapid}$$

$$A + K \rightleftarrows C \quad \text{rapid}$$

$$C + A \rightarrow P \quad \text{rate-determining} \quad . \tag{18}$$

The assumptions in analyzing the data according to mechanism (18) are the following. The aluminum alkyl is present predominantly as monomer. The formation of the complex C, from the reactants is rapid and complete. The rate controlling step involves attack of the trimethylaluminum monomer on the complex to give product. The product holds a molecule of trimethylaluminum.

The differential equation expressing the disappearance of the complex according to mechanism (18) is given by (19):

$$\frac{dC}{dt} = - kC(C+A-2K) \quad , \tag{19}$$

where C is the complex at time t, A is the analytically measured amount of trimethylaluminum, and K is the initial concentration of benzophenone. The solution to equation (19) is given by (20):

$$k = \frac{2.3}{t(A-2K)} \log \frac{C_o(C+A-2K)}{C(C_o+A-2K)} \quad , \tag{20}$$

where $C_o$ is the concentration of complex at zero reaction time. For the special case where A = 2K the differential equation expressing the disappearance of complex is given by (21):

$$\frac{dC}{dt} = kC^2 \quad . \tag{21}$$

The solution to equation (21) is given by (22):

$$k = \frac{1}{t}\left(\frac{1}{C} - \frac{1}{C_o}\right) \quad . \tag{22}$$

Complete derivations of equations (20) and (22) can be found in the Appendix, Derivation 4. The results of the calculations are shown in Table 5.

Evaluation of the Data and Choice of Mechanism

The constants calculated from the Dimer-Dimer analysis and from the Dimer-Monomer analysis are given in Table 4. The data in Table 4 are arranged according to increasing $(CH_3)_3Al$ to $(C_6H_5)_2CO$ ratio. Although the rate constants calculated from the Dimer-Dimer analysis are consistent within a given run values from different runs were found to be dependent on the trimethylaluminum to benzophenone ratio. As the ratio of trimethylaluminum to benzophenone increases, the rate constants decrease. At the lowest $(CH_3)_3Al$:$(C_6H_5)_2CO$ studied, 1.54:1, the average rate constant is 5.00 ± 0.30 l mole$^{-1}$ sec$^{-1}$, while at the highest ratio studied, 3.76:1, the average rate constant is only 3.24 ± 0.22 l mole$^{-1}$ sec$^{-1}$. The average

deviation for each rate constant indicates the consistency during a particular run. This unmistakable trend to lower rate constants with aluminum alkyl to ketone ratios suggest that the Dimer-Dimer analysis does not properly describe the system.

The constants calculated from the Dimer-Monomer analysis provide a better fit to the data than those calculated from the Dimer-Dimer analysis. The average constants calculated for the former show no trend with the trimethylaluminum to benzophenone ratio if that ratio is 2:1 or greater. At ratios of $(CH_3)_3Al$ to $(C_6H_5)_2CO$ of less than 2:1 the constants were somewhat smaller than those calculated for the reactant ratios greater than 2:1. This trend is not dependent solely on reactant ratio. In those runs in which the trimethylaluminum to benzophenone ratio is exactly 2:1, the tendency toward a smaller average constant is found when the initial trimethylaluminum concentration is 0.00755 M or less, but not found when the initial concentration of trimethylaluminum is 0.0113 M. In those cases in which a smaller average constant was found from the Dimer-Monomer analysis, a trend toward decreasing constants with reaction time was found for individual runs. In all runs where this occurred the concentration of the free trimethylaluminum was equal to or less than the amount of complex initially formed so that at 100 percent reaction no free aluminum alkyl exist. The values calculated for the initial part of the run where constants decreased with increasing reaction time are about the same in magnitude as the constants calculated when the initial amount of free aluminum alkyl exceeds the initial amount of complex. A run which shows decreasing constants with increasing reaction time is illustrated in Figure 3.

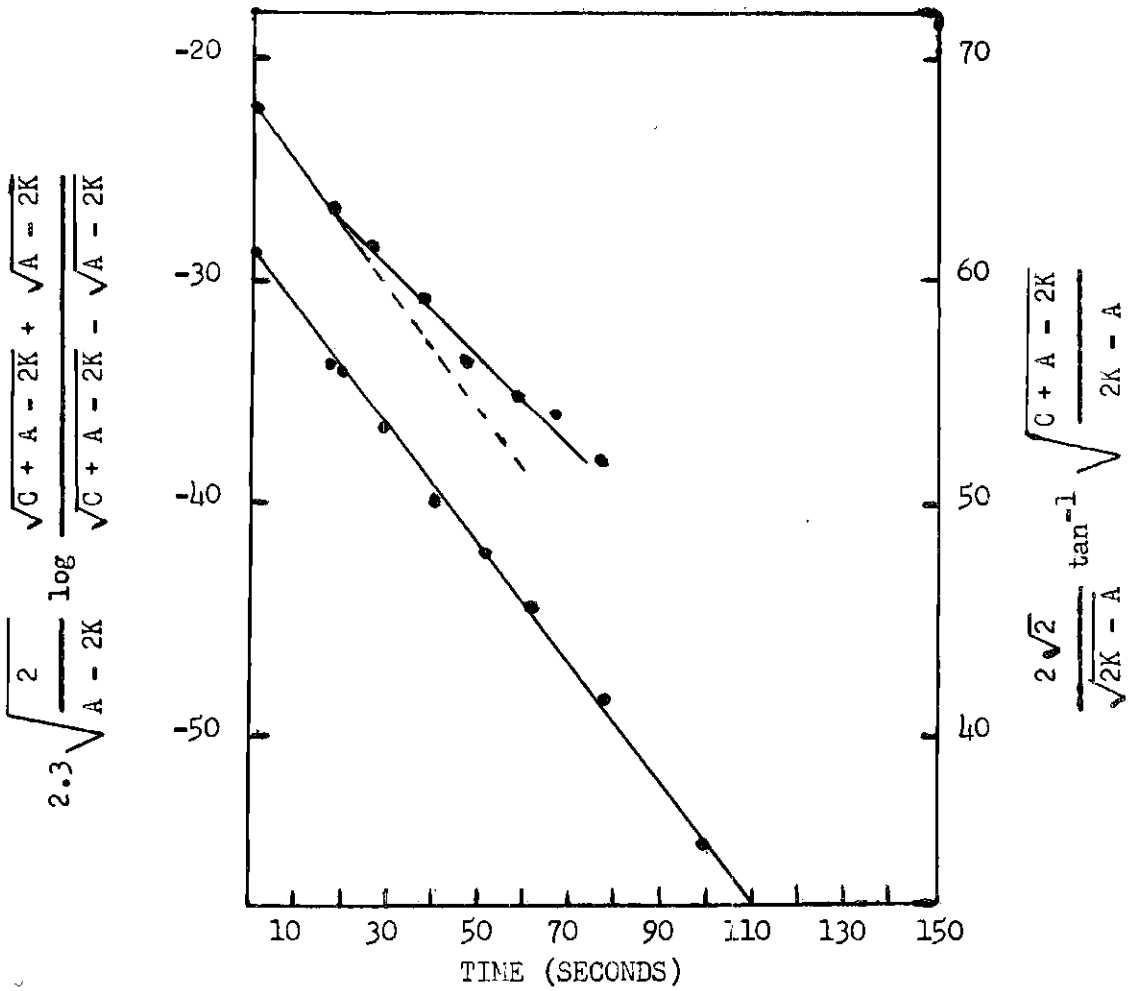



Figure 3. Graphical Test of the Dimer-Monomer Mechanism According to Equations (14) and (15). (Data from Table 25 and Table 34 in Appendix for Upper and Lower Curves Respectively.)

The trends found for constants calculated from the Dimer-Monomer analysis suggest that at low trimethylaluminum concentration a considerable proportion of trimethylaluminum exist as monomer. As mentioned previously, in those runs in which the amount of free trimethylaluminum is equal to or less than the amount of complex, the concentration of free trimethylaluminum is very small near the end of the reaction. Thus, as the reaction progresses the proportion of trimethylaluminum monomer increases. It is possible to determine approximately the concentration of aluminum alkyl in which the amount of monomer is significant enough to cause decreasing constants. Table 29 in the Appendix shows a run in which the initial concentration of free aluminum alkyl is 0.01156 and the $(CH_3)_3Al:(C_6H_5)_2CO$ ratio is 2:1. The reaction was followed through 71 percent and no decrease in the constant calculated was noted. Thus, at 0.29 x 0.01156 M = .00335 M the aluminum alkyl exist largely as dimer. Table 30 in the Appendix shows a run in which the initial concentration of free aluminum alkyl is 0.00602 and the $(CH_3)_3Al:(C_6H_5)_2CO$ ratio is 2:1. At 52 percent reaction the first real decrease can be seen in the calculated constant. Thus, at 0.48 x 0.00602 M = .00282 M the amount of aluminum alkyl which exist as monomer begins to influence the constant calculated from the Dimer-Monomer analysis.

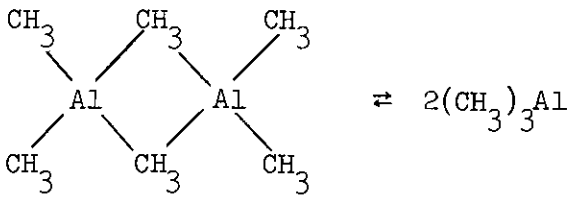
Table 5 compares constants calculated from the Dimer-Monomer analysis with rate constants calculated from the Monomer-Monomer analysis. The data in Table 5 are arranged according to increasing free trimethylaluminum concentration. The average constants marked with an asterisk are those in which the run from which the average constant was calculated showed a trend in the constant with reaction time. The constants calculated from

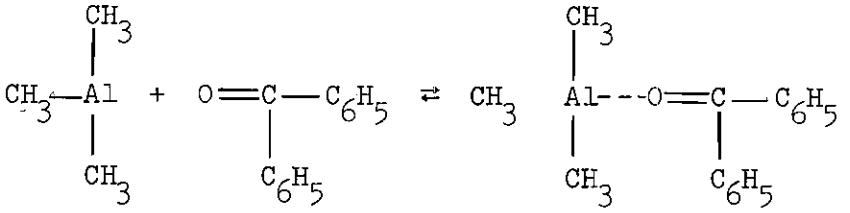
the Dimer-Monomer analysis show a tendency to decrease with increasing reaction time only when the ratio of aluminum alkyl to ketone is 2:1 or less and when the initial concentration of free aluminum alkyl is less than .0076 M. The rate constants calculated from the Monomer-Monomer analysis showed a tendency to increase with reaction time when the ratio of trimethylaluminum to benzophenone is 2:1 or greater and when the initial concentration of free trimethylaluminum is .006 M or greater. The average rate constants from the Monomer-Monomer analysis also decrease with increasing ratio due to the high proportion of dimer in these reactions.

The sixth row of figures in Table 5 represent constants calculated from the Dimer-Monomer analysis for 50 percent reaction for those runs in which decreasing constants with increasing reaction time were found. These constants are much closer to those calculated for the case in which the amount of free trimethylaluminum is greater than the initial amount of complex. The fact that they are still somewhat low indicates that in the region where the concentration of trimethylaluminum is 0.005 M or less, enough trimethylaluminum exist as monomer to influence the constant.

The reaction of trimethylaluminum with benzophenone to give product proceeds by the monomer mechanism. At high free aluminum alkyl concentrations the predominant aluminum alkyl species is the dimer and at low aluminum alkyl concentration the aluminum alkyl exist largely as monomer. Regardless of the trimethylaluminum monomer: dimer ratio, the rate controlling step of the reaction is an attack of monomeric trimethylaluminum on the complex. This is indeed the preferred reaction path when it is operative. The details of this mechanism are represented by the following

equations:





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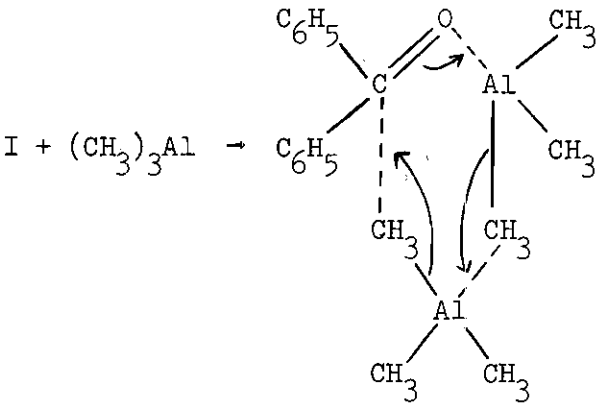
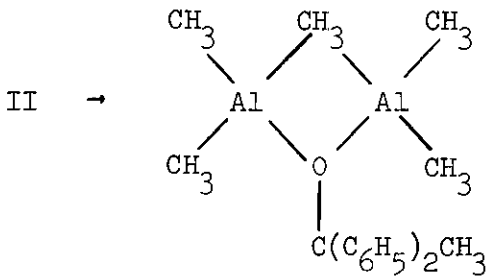


II



Reaction of Benzophenone with Trimethylaluminum in Diethyl Ether

The reaction between trimethylaluminum and benzophenone in ether was found to be very slow. When trimethylaluminum was allowed to react with benzophenone in a 2.7:1 ratio, only 80 percent of the ketone had reacted after four weeks. Ultraviolet analysis indicates that the principal reason for the sluggishness of this reaction in ether is the fact that little complexation occurs. When large excesses of trimethylaluminum were added to benzophenone the ketone spectra changed little. A kinetic run in which a large excess of the organoaluminum compound was used showed the reaction is first-order in benzophenone.

In ether the reaction of trimethylaluminum with complex to form product may not be operative. This is due to the fact that ether strongly complexes trimethylaluminum. In any case it is obvious that more work needs to be performed on this system before mechanistic conclusions can be made.

# CHAPTER IV

## CONCLUSIONS

The first successful kinetics of the reaction of trimethylaluminum with benzophenone in benzene have been studied. The reaction was studied at trimethylaluminum to benzophenone ratios of .855:1 to 3.76:1 which was the widest range allowed by the nature of the reaction. The large difference in the rate between the reaction when the amount of trimethylaluminum is equivalent to or less than the ketone and when excess trimethylaluminum is used suggest the possibility of two different mechanisms.

When equivalent amounts of trimethylaluminum and benzophenone are used the mechanism is best represented by a rapid formation of a complex from the reactants followed by an internal transfer of a methyl group to give product. The kinetics are complicated by the fact that the product initially formed can complex further trimethylaluminum. The equilibrium constant governing the formation of the complex is very large.

$$A_2 \rightleftarrows 2A \quad \text{rapid}$$

$$A + K \rightleftarrows C \quad \text{rapid}$$

$$C \rightarrow P' \quad \text{rate-determining}$$

$$P' + A \rightleftarrows P \quad \text{rapid}$$

When excess trimethylaluminum is used the reaction is very rapid and the preferred mechanism is operative. This mechanism involves the

formation of a complex from the reactants followed by a rapid attack of trimethylaluminum monomer to give the product. The equilibrium constant governing the formation of the complex is so large that for mathematical purposes no free ketone exists once the reactants are mixed. The best proof offered to date for the large value of an equilibrium constant is the precision of the data presented here.

$$A_2 \overset{K_D}{\rightleftharpoons} 2A \quad \text{rapid}$$

$$A + K \rightleftharpoons C \quad \text{rapid}$$

$$C + A \overset{k}{\rightarrow} P \quad \text{rate-determining}$$

The reaction of trimethylaluminum with benzophenone in diethyl ether is very slow. Ultraviolet spectral data indicates the reason for this is the fact that little complex is formed due to the competition of diethyl ether with the ketone for the aluminum alkyl.

# APPENDIX

Derivation 1. Derivation of the Rate Equation for the Reaction of Trimethylaluminum with Equivalent Benzophenone. Decrease of the Carbonyl Band at 345 mμ.

Mechanism

$$A_2 \rightleftarrows 2_A \quad \text{rapid}$$

$$A + K \rightleftarrows C \quad \text{rapid}$$

$$C \xrightarrow{k} P' \quad \text{rate controlling}$$

$$P' + A \rightarrow P \quad \text{rapid and complete}$$

Definitions

$K_o$ = initial concentration of benzophenone

$K$ = concentration of benzophenone at time t

$A_o$ = the initial concentration of trimethylaluminum, expressed as monomer

$C$ = concentration of complex at time t

$x$ = experimental variable = $K + C$

Assumptions

1. The equilibrium constant governing the formation of the complex is very large, so that concentrations of $\left(Al(CH_3)_3\right)_2$ and $Al(CH_3)_3$ are negligible.
2. Step four occurs rapidly and completely so that the concentration of P is negligible.

Conditions

$$K_o = A_o$$

$$K_o = C + P' + K = x + P'$$

$$A_o = C + 2P'$$

Derivation

$$C + P' + K = K_o = A_o = C + 2P'$$

therefore,

$$K = P'$$

$$2K_o - A_o = K_o = 2X - C$$

$$C = 2X - K_o$$

The proper differential equation in terms of the variable X is given by (1)

$$\frac{dX}{dt} = -\frac{dP'}{dt} = -kC = -2k(X - \tfrac{1}{2}K_o) \qquad (1)$$

The solution to Equation (1) is given by (2)

$$k' = 2k = \frac{2.3}{t} \log \frac{X_o - \frac{1}{2}K_o}{X - \frac{1}{2}K_o} \qquad (2)$$

For purposes of calculation,

$$k' = \frac{2.3}{t} \log \frac{K_o - \frac{1}{2}K_o}{X - \frac{1}{2}K_o}$$

$$k' = \frac{2.3}{t} \log \frac{K_o - K_o + \frac{1}{2}A_o}{X - K_o + \frac{1}{2}A_o} \quad .$$

Noting that

$$\frac{dC}{dt} = 2\frac{dX}{dt} = -2kC$$

hence,

$$k_{obs} = 2k = k' \quad .$$

Derivation 2. Derivation of the Rate Equation for the Dimer-Dimer Analysis

Mechanism

$$A_2 \rightleftarrows 2A \quad \text{rapid}$$

$$A + K \rightleftarrows C \quad \text{rapid}$$

$$C + A_2 \overset{k_d}{\rightleftarrows} P + A \quad \text{rate controlling}$$

Definitions

$K$ = initial benzophenone concentration

$A$ = initial trimethylaluminum concentration as monomer

$A_2$ = trimethylaluminum dimer

$C_o$ = initial concentration of complex

$C$ = concentration of complex at time t

$P$ = reaction product

Assumptions

1. Trimethylaluminum is present predominately as dimer
2. Upon mixing the reagents the complex is formed immediately and no uncomplexed benzophenone exists
3. The rate controlling step of the reaction is definitely $k_d$

Conditions

$$K = C + P$$

$$A = C + 2P + A_2$$

Derivation

$$2K - A = C - 2A_2$$

$$2A_2 = C + A - 2K$$

$$A_2 = \tfrac{1}{2}(C + A - 2K)$$

The proper differential equation expressing the disappearance of complex is given by (3)

$$\frac{dC}{dt} = -\frac{dP}{dt}$$

$$\frac{dC}{dt} = -\frac{k_d}{2} C(C+A-2K) \qquad (3)$$

The solution to Equation (3) is given by (4)

$$k_d = \frac{2 \times 2.3}{t(A - 2K)} \log \frac{C_o(C+A-2K)}{C(C_o+A-2K)} \qquad (4)$$

For the special case where A = 2K, the proper differential equation is given by (5)

$$\frac{dC}{dt} = \tfrac{1}{2}k_d C^2 \qquad (5)$$

The solution to Equation (5) is given by Equation (6)

$$k_d = \frac{2}{t}\left(\frac{1}{C} - \frac{1}{C_o}\right) \qquad (6)$$

Derivation 3. Derivation of the Rate Equation for the Dimer-Monomer Analysis

Mechanism

$$A_2 \overset{K_D}{\rightleftarrows} 2A \quad \text{rapid}$$

$$A + K \rightleftarrows C \quad \text{rapid}$$

$$C + A \overset{k}{\rightleftarrows} P \quad \text{rate controlling}$$

Definitions

$A_2$ = dimeric trimethylaluminum

$A$ = trimethylaluminum calculated as monomer

$K$ = initial concentration of benzophenone

$C_o$ = initial concentration of complex

$C$ = concentration of complex at time t

$P$ = reaction product

$K_D$ = dissociation constant for trimethylaluminum in benzene at 25°C

Assumptions

1. Trimethylaluminum is present predominately as dimer
2. Upon mixing the reagents the complex is formed immediately and no uncomplexed benzophenone exists
3. The rate controlling step is definitely k

Conditions

$$K_D = \frac{A^2}{A_2}$$

$$A = \sqrt{K_D}\, A_2^{\frac{1}{2}}$$

$$K = C + P$$

$$A = C + 2P + 2A_2$$

Derivation

$$2K - A = C - 2A_2$$

$$A_2 = \tfrac{1}{2}(C+A-2K)$$

$$A = \frac{\sqrt{K_D}}{2}(C+A-2K)^{\frac{1}{2}}$$

$$\frac{dC}{dt} = -\frac{dP}{dt}$$

The proper differential equation expressing the disappearance of complex is given by (7)

$$\frac{dC}{dt} = \frac{k\sqrt{K_D}}{2} C(C+A-2K)^{\frac{1}{2}} \tag{7}$$

Equation (7) has two solutions. If A is greater than 2K the solution is given by (8)

$$k\sqrt{K_D} = \frac{2.3\sqrt{2}}{t\sqrt{A-2K}} \log \frac{\left(\sqrt{C_o+A-2K} - \sqrt{A-2K}\right)\left(\sqrt{C+A-2K} + \sqrt{A-2K}\right)}{\left(\sqrt{C_o+A-2K} + \sqrt{A-2K}\right)\left(\sqrt{C+A-2K} - \sqrt{A-2K}\right)} \tag{8}$$

If A is less than 2K the solution is given by (9)

$$k\sqrt{K_D} = \frac{2\sqrt{2}}{t\sqrt{2K-A}} \left( \tan^{-1}\sqrt{\frac{C_o+A-2K}{2K-A}} - \tan^{-1}\sqrt{\frac{C+A-2K}{2K-A}} \right). \tag{9}$$

For the special case where A = 2K the proper differential equation is given by (10)

$$\frac{dC}{dt} = -\frac{k\sqrt{K_D}}{\sqrt{2}} C^{3/2} . \tag{10}$$

The solution to Equation (10) is given by (11)

$$k\sqrt{K_D} = \frac{2\sqrt{2}}{t}\left(\frac{1}{\sqrt{C}} - \frac{1}{\sqrt{C_o}}\right) \quad . \tag{11}$$

## Derivation 4. Derivation of the Rate Equation for the Monomer-Monomer Analysis

Mechanism

$$A_2 \rightleftarrows 2A \quad \text{rapid}$$

$$A + K \rightleftarrows C \quad \text{rapid}$$

$$C + A \xrightarrow{k} P \quad \text{rate controlling}$$

Definitions

$A_2$ = dimeric trimethylaluminum

A = Trimethylaluminum calculated as monomer

K = initial concentration of benzophenone

$C_o$ = initial concentration of complex

C = concentration of complex at time t

P = reaction product

Assumptions

1. Trimethylaluminum is present predominately as monomer
2. Upon mixing the reagents the complex is formed immediately and no uncomplexed benzophenone exists
3. The rate controlling step is definitely k

Conditions

$$K = C + P$$

$$A = C + 2P + A$$

Derivation

$$2K - A = C - A$$

$$A = C + A - 2K$$

The proper differential equation expressing the disappearance of complex is given by (12)

$$\frac{dC}{dt} = - \frac{dP}{dt}$$

$$\frac{dC}{dt} = - kC(C + A - 2K) \qquad (12)$$

The solution to Equation (12) is given by (13)

$$k = \frac{2.3}{t(A-2K)} \log \frac{C_o(C+A-2K)}{C(C_o+A-2K)} \quad . \qquad (13)$$

For the special case where A = 2K, the proper differential equation is given by (14)

$$\frac{dC}{dt} = kC^2 \quad . \qquad (14)$$

The solution to Equation (14) is given by (15)

$$k = \frac{1}{t}\left(\frac{1}{C} - \frac{1}{C_o}\right) \quad . \qquad (15)$$

Table 6. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Complex Band at 412 mμ.

| Time Seconds | Absorbance | $10^4 k_{obs}$ [a] $sec^{-1}$ |
|---|---|---|
| 0 | 1.605 | |
| 500 | 1.432 | 2.30 |
| 1000 | 1.270 | 2.30 |
| 1500 | 1.114 | 2.42 |
| 2000 | 0.990 | 2.43 |
| 2500 | 0.860 | 2.50 |
| 3000 | 0.772 | 2.44 |
| 3500 | 0.669 | 2.51 |
| 4000 | 0.581 | 2.53 |

Avg. 2.44 ± 0.09

Initial Concentrations

Benzophenone . . . . . $6.58 \times 10^{-3}$ M

Trimethylaluminum[b] . . . . . $6.60 \times 10^{-3}$ M

[a] Calculated from Equation (2)

[b] By dilution

Table 7. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Complex Band at 412 mμ.

| Time Seconds | Absorbance | $10^4 k_{obs}$ [a] $sec^{-1}$ |
|---|---|---|
| 0 | 1.590 | |
| 300 | 1.476 | 2.47 |
| 500 | 1.405 | 2.48 |
| 800 | 1.297 | 2.55 |
| 1000 | 1.230 | 2.58 |
| 1300 | 1.131 | 2.64 |
| 1500 | 1.070 | 2.62 |
| 1800 | 0.995 | 2.58 |
| 2000 | 0.940 | 2.64 |
| 2300 | 0.870 | 2.64 |
| 2500 | 0.815 | 2.69 |
| 2800 | 0.767 | 2.62 |
| 3000 | 0.725 | 2.62 |
| 3300 | 0.668 | 2.64 |
| 3500 | 0.631 | 2.64 |
| 3800 | 0.581 | 2.59 |
| 4000 | 0.551 | 2.67 |
| 4300 | 0.512 | 2.64 |
| 4500 | 0.492 | 2.62 |
| 4800 | 0.449 | 2.64 |
| 5000 | 0.423 | 2.67 |
| 5500 | 0.378 | 2.62 |
| 6000 | 0.352 | 2.53 |
| | | Avg. 2.55 ± 0.03 |

Initial Concentrations

Benzophenone . . . . . $6.58 \times 10^{-3}$ M

Trimethylaluminum[b] . . . . . $6.60 \times 10^{-3}$ M

[a] Calculated from Equation (2)

[b] By dilution

Table 8. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Complex Band at 412 mμ.

| Time Seconds | Absorbance | $10^4 k_{obs}$ [a] $sec^{-1}$ |
|---|---|---|
| 0 | 1.504 | |
| 300 | 1.400 | 2.46 |
| 500 | 1.400 | 2.46 |
| 800 | 1.240 | 2.42 |
| 1000 | 1.101 | 2.44 |
| 1300 | 1.102 | 2.42 |
| 1500 | 1.046 | 2.42 |
| 1800 | 0.970 | 2.45 |
| 2000 | 0.920 | 2.48 |
| 2300 | 0.834 | 2.56 |
| 2500 | 0.794 | 2.56 |
| 2800 | 0.744 | 2.51 |
| 3000 | 0.685 | 2.63 |
| 3200 | 0.655 | 2.60 |
| 3500 | 0.613 | 2.56 |
| 3800 | 0.556 | 2.61 |
| 4000 | 0.542 | 2.55 |
| 4300 | 0.498 | 2.57 |
| 4500 | 0.472 | 2.57 |
| 5000 | 0.418 | 2.56 |
| 6000 | 0.330 | 2.53 |
| | | Avg. 2.49 ± 0.07 |

Initial Concentrations

Benzophenone . . . . . $6.58 \times 10^{-3}$ M

Trimethylaluminum[b] . . . . . $6.60 \times 10^{-3}$ M

[a] Calculated from Equation (2)

[b] By dilution

Table 9. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Complex Band at 412 mμ.

| Time Seconds | Absorbance | $10^4 k_{obs}$ [a] $sec^{-1}$ |
|---|---|---|
| 0 | 1.420 | |
| 300 | 1.332 | 2.14 |
| 500 | 1.275 | 2.18 |
| 800 | 1.183 | 2.30 |
| 1000 | 1.124 | 2.35 |
| 1300 | 1.051 | 2.32 |
| 1500 | 1.000 | 2.34 |
| 1800 | 0.935 | 2.32 |
| 2000 | 0.882 | 2.39 |
| 2300 | 0.821 | 2.38 |
| 2500 | 0.780 | 2.40 |
| 2800 | 0.727 | 2.39 |
| 3000 | 0.694 | 2.39 |
| 3300 | 0.645 | 2.40 |
| 3500 | 0.618 | 2.38 |
| 3800 | 0.575 | 2.38 |
| 4000 | 0.553 | 2.36 |
| 4300 | 0.517 | 2.35 |
| 4500 | 0.496 | 2.39 |
| 4800 | 0.465 | 2.34 |
| 5000 | 0.446 | 2.33 |
| 5300 | 0.420 | 2.31 |
| 5500 | 0.406 | 2.28 |
| 5800 | 0.386 | 2.25 |
| 6000 | 0.373 | 2.24 |
| | | Avg. 2.32 ± 0.05 |

Initial Concentrations
Benzophenone . . . . . $6.91 \times 10^{-3}$ M
Trimethylaluminum[b] . . . . . $6.90 \times 10^{-3}$ M

[a] Calculated from Equation (2)
[b] By analysis

Table 10. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Complex Band at 412 mμ.

| Time Seconds | Absorbance | $10^4 k_{obs}$ [a] $sec^{-1}$ |
|---|---|---|
| 0 | 1.503 | |
| 300 | 1.406 | 2.30 |
| 500 | 1.350 | 2.17 |
| 800 | 1.256 | 2.25 |
| 1000 | 1.194 | 2.30 |
| 1300 | 1.110 | 2.34 |
| 1500 | 1.058 | 2.35 |
| 1800 | 0.981 | 2.38 |
| 2000 | 0.940 | 2.35 |
| 2300 | 0.870 | 2.38 |
| 2500 | 0.818 | 2.44 |
| 2800 | 0.775 | 2.37 |
| 3000 | 0.739 | 2.36 |
| 3300 | 0.682 | 2.40 |
| 3500 | 0.651 | 2.39 |
| 3800 | 0.609 | 2.38 |
| 4000 | 0.578 | 2.40 |
| 4300 | 0.541 | 2.38 |
| 4500 | 0.527 | 2.34 |
| 4800 | 0.483 | 2.38 |
| 5000 | 0.463 | 2.36 |
| 5300 | 0.436 | 2.34 |
| 5500 | 0.420 | 2.32 |
| 5800 | 0.399 | 2.30 |
| 6000 | 0.374 | 2.32 |
| Initial Concentrations | | Avg. 2.35 ± 0.04 |
| Benzophenone [b] . . . . . | $6.91 \times 10^{-3}$ M | |
| Trimethylaluminum [b] . . . . . | $6.90 \times 10^{-3}$ M | |

a Calculated from Equation (2)
b By analysis

Table 11. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Complex Band at 412 mμ.

| Time Seconds | Absorbance | $10^4 k_{obs}$ [a] $sec^{-1}$ |
|---|---|---|
| 0 | 1.495 | |
| 300 | 1.397 | 2.31 |
| 500 | 1.334 | 2.30 |
| 800 | 1.236 | 2.42 |
| 1000 | 1.176 | 2.39 |
| 1300 | 1.088 | 2.46 |
| 1500 | 1.033 | 2.47 |
| 1800 | 0.970 | 2.40 |
| 2000 | 0.920 | 2.44 |
| 2300 | 0.850 | 2.45 |
| 2500 | 0.808 | 2.46 |
| 2800 | 0.753 | 2.45 |
| 3000 | 0.719 | 2.44 |
| 3300 | 0.665 | 2.45 |
| 3500 | 0.622 | 2.51 |
| 3800 | 0.588 | 2.47 |
| 4000 | 0.540 | 2.50 |
| 4300 | 0.535 | 2.34 |
| 4500 | 0.515 | 2.37 |
| 4800 | 0.473 | 2.40 |
| 5000 | 0.451 | 2.40 |
| 5300 | 0.423 | 2.39 |
| 5500 | 0.404 | 2.39 |
| 5800 | 0.389 | 2.32 |
| 6000 | 0.373 | 2.32 |
| Initial Concentrations | | Avg. 2.41 ± 0.04 |
| Benzophenone [b] . . . . . | $6.91 \times 10^{-3}$ M | |
| Trimethylaluminum [b] . . . . . | $6.90 \times 10^{-3}$ M | |

[a] Calculated from Equation (2)
[b] By analysis

Table 12. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Complex Band at 412 mμ.

| Time Seconds | Absorbance | $10^4 k_{obs}$ [a] $sec^{-1}$ |
|---|---|---|
| 0 | 2.120 | |
| 300 | 1.983 | 2.30 |
| 500 | 1.895 | 2.27 |
| 800 | 1.765 | 2.30 |
| 1000 | 1.685 | 2.28 |
| 1300 | 1.564 | 2.30 |
| 1500 | 1.490 | 2.35 |
| 1800 | 1.381 | 2.34 |
| 2000 | 1.315 | 2.38 |
| 2300 | 1.223 | 2.39 |
| 2500 | 1.168 | 2.39 |
| 2800 | 1.074 | 2.39 |
| 3000 | 1.033 | 2.39 |
| 3300 | 0.961 | 2.33 |
| 3500 | 0.918 | 2.39 |
| 3800 | 0.860 | 2.37 |
| 4000 | 0.820 | 2.38 |
| 4300 | 0.770 | 2.36 |
| 4500 | 0.731 | 2.37 |
| 4800 | 0.685 | 2.35 |
| 5000 | 0.662 | 2.34 |
| 5300 | 0.620 | 2.32 |
| 5500 | 0.595 | 2.31 |
| 5800 | 0.560 | 2.30 |
| 6000 | 0.538 | 2.29 |
| Initial Concentrations | | Avg. 2.33 ± 0.04 |
| Benzophenone . . . . . | $9.11 \times 10^{-3}$ M | |
| Trimethylaluminum[b] . . . . . | $8.90 \times 10^{-3}$ M | |

[a] Calculated from Equation (2)

[b] By analysis

Table 13. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Complex Band at 412 mμ.

| Time Seconds | Absorbance | $10^4 k_{obs}$ [a] $sec^{-1}$ |
|---|---|---|
| 0 | 2.060 | |
| 300 | 1.920 | 2.37 |
| 500 | 1.830 | 2.39 |
| 800 | 1.699 | 2.41 |
| 1000 | 1.610 | 2.48 |
| 1300 | 1.477 | 2.54 |
| 1500 | 1.412 | 2.52 |
| 1800 | 1.315 | 2.49 |
| 2000 | 1.241 | 2.54 |
| 2300 | 1.154 | 2.52 |
| 2500 | 1.092 | 2.54 |
| 2800 | 1.020 | 2.51 |
| 3000 | 0.961 | 2.54 |
| 3300 | 0.898 | 2.51 |
| 3500 | 0.850 | 2.52 |
| 3800 | 0.780 | 2.56 |
| 4000 | 0.753 | 2.52 |
| 4300 | 0.698 | 2.46 |
| 4500 | 0.665 | 2.52 |
| 4800 | 0.622 | 2.49 |
| 5000 | 0.596 | 2.48 |
| 5300 | 0.558 | 2.47 |
| 5500 | 0.530 | 2.47 |
| 5800 | 0.501 | 2.54 |
| 6000 | 0.485 | 2.41 |
| Initial Concentrations | | Avg. 2.50 ± 0.04 |
| Benzophenone | $9.11 \times 10^{-3}$ M | |
| Trimethylaluminum [b] | $8.90 \times 10^{-3}$ M | |

[a] Calculated from Equation (2)

[b] By analysis

Table 14. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Complex Band at 412 mμ.

| Time Seconds | Absorbance | $10^4 k_{obs}$ [a] $sec^{-1}$ |
|---|---|---|
| 0 | 2.120 | |
| 300 | 1.978 | 2.48 |
| 500 | 1.890 | 2.35 |
| 800 | 1.750 | 2.41 |
| 1000 | 1.668 | 2.42 |
| 1300 | 1.546 | 2.44 |
| 1500 | 1.474 | 2.42 |
| 1800 | 1.364 | 2.46 |
| 2000 | 1.290 | 2.48 |
| 2300 | 1.197 | 2.48 |
| 2500 | 1.127 | 2.52 |
| 2800 | 1.062 | 2.46 |
| 3000 | 1.011 | 2.47 |
| 3300 | 0.943 | 2.45 |
| 3500 | 0.898 | 2.45 |
| 3800 | 0.840 | 2.43 |
| 4000 | 0.790 | 2.46 |
| 4300 | 0.744 | 2.48 |
| 4500 | 0.715 | 2.43 |
| 4800 | 0.655 | 2.44 |
| 5000 | 0.630 | 2.43 |
| 5300 | 0.592 | 2.40 |
| 5500 | 0.570 | 2.39 |
| 5800 | 0.540 | 2.36 |
| 6000 | 0.524 | 2.33 |
| Initial Concentrations | | Avg. 2.43 ± 0.03 |
| Benzophenone . . . . . | $9.11 \times 10^{-3}$ M | |
| Trimethylaluminum[b] . . . . . | $8.90 \times 10^{-3}$ M | |

[a] Calculated from Equation (2)

[b] By analysis

Table 15. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Complex Band at 412 mμ.

| Time Seconds | Absorbance | $10^4 k_{obs}$ [a] $sec^{-1}$ |
|---|---|---|
| 0 | 0.860 | |
| 300 | 0.800 | 2.45 |
| 500 | 0.766 | 2.30 |
| 800 | 0.711 | 2.39 |
| 1000 | 0.679 | 2.36 |
| 1300 | 0.632 | 2.37 |
| 1500 | 0.600 | 2.40 |
| 1800 | 0.557 | 2.41 |
| 2000 | 0.531 | 2.41 |
| 2300 | 0.492 | 2.42 |
| 2500 | 0.470 | 2.41 |
| 2800 | 0.435 | 2.43 |
| 3000 | 0.414 | 2.44 |
| 3300 | 0.384 | 2.44 |
| 3500 | 0.366 | 2.44 |
| 3800 | 0.338 | 2.46 |
| 4000 | 0.317 | 2.49 |
| 4300 | 0.298 | 2.46 |
| 4500 | 0.282 | 2.48 |
| 4800 | 0.261 | 2.48 |
| 5000 | 0.251 | 2.47 |
| 5300 | 0.241 | 2.40 |
| 5500 | 0.217 | 2.50 |
| 5800 | 0.210 | 2.43 |
| 6000 | 0.203 | 2.41 |
| Initial Concentrations | | Avg. 2.42 ± 0.03 |
| Benzophenone . . . . . | $4.44 \times 10^{-3}$ M | |
| Trimethylaluminum[b] . . . . . | $4.15 \times 10^{-3}$ M | |

[a] Calculated from Equation (2)

[b] By analysis

Table 16. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Complex Band at 412 mμ.

| Time Seconds | Absorbance | $10^4 k_{obs}$ [a] $sec^{-1}$ |
|---|---|---|
| 0 | 0.840 | |
| 300 | 0.789 | 2.14 |
| 500 | 0.755 | 2.16 |
| 800 | 0.711 | 2.07 |
| 1000 | 0.660 | 2.41 |
| 1300 | 0.618 | 2.47 |
| 1500 | 0.589 | 2.48 |
| 1800 | 0.548 | 2.36 |
| 2000 | 0.512 | 2.46 |
| 2300 | 0.470 | 2.52 |
| 2500 | 0.455 | 2.44 |
| 2800 | 0.415 | 2.52 |
| 3000 | 0.396 | 2.50 |
| 3300 | 0.365 | 2.46 |
| 3500 | 0.350 | 2.43 |
| 3800 | 0.325 | 2.50 |
| 4000 | 0.307 | 2.52 |
| 4300 | 0.285 | 2.50 |
| 4500 | 0.260 | 2.61 |
| 4800 | 0.245 | 2.57 |
| 5000 | 0.238 | 2.52 |
| 5300 | 0.225 | 2.48 |
| 5500 | 0.205 | 2.56 |
| 5800 | 0.200 | 2.48 |
| 6000 | 0.189 | 2.49 |
| Initial Concentrations | | Avg. 2.41 ± 0.12 |
| Benzophenone . . . . . | $4.44 \times 10^{-3}$ M | |
| Trimethylaluminum[b] . . . . . | $4.15 \times 10^{-3}$ M | |

[a] Calculated from Equation (2)

[b] By analysis

Table 17. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Complex Band at 412 mμ.

| Time Seconds | Absorbance | $10^4 k_{obs}$ [a] $sec^{-1}$ |
|---|---|---|
| 0 | 0.840 | |
| 300 | 0.791 | 2.07 |
| 500 | 0.757 | 2.12 |
| 800 | 0.701 | 2.24 |
| 1000 | 0.671 | 2.25 |
| 1300 | 0.620 | 2.34 |
| 1500 | 0.589 | 2.38 |
| 1800 | 0.540 | 2.45 |
| 2000 | 0.512 | 2.47 |
| 2300 | 0.475 | 2.48 |
| 2500 | 0.449 | 2.50 |
| 2800 | 0.415 | 2.51 |
| 3000 | 0.395 | 2.51 |
| 3300 | 0.369 | 2.48 |
| 3500 | 0.349 | 2.51 |
| 3800 | 0.326 | 2.49 |
| 4000 | 0.304 | 2.54 |
| 4300 | 0.276 | 2.59 |
| 4500 | 0.267 | 2.54 |
| 4800 | 0.250 | 2.52 |
| 5000 | 0.234 | 2.54 |
| 5300 | 0.223 | 2.50 |
| 5500 | 0.215 | 2.48 |
| 5800 | 0.196 | 2.51 |
| 6000 | 0.189 | 2.48 |
| Initial Concentrations | | Avg. 2.41 ± 0.11 |
| Benzophenone . . . . . | $4.44 \times 10^{-3}$ M | |
| Trimethylaluminum[b] . . . . . | $4.15 \times 10^{-3}$ M | |

[a] Calculated from Equation (2)

[b] By analysis

Table 18. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $10^4 k'$,[a] $sec^{-1}$ |
|---|---|---|
| 50 | 2.040 | |
| 1001 | 1.875 | 2.05 |
| 2010 | 1.731 | 2.16 |
| 3007 | 1.631 | 2.10 |
| 3997 | 1.558 | 2.02 |
| 5000 | 1.476 | 2.08 |
| 5992 | 1.443 | 1.90 |
| 8165 | 1.310 | 2.22 |
| 10007 | 1.225 | |
| 11994 | 1.160 | |
| 14009 | 1.100 | |
| 16003 | 1.061 | |
| 14009 | 1.100 | |
| 16003 | 1.061 | |
| 18005 | 1.020 | |
| 86000 | 0.730 | |

Avg. 2.09 ± 0.08

Initial Concentrations

Benzophenone . . . . . $16.05 \times 10^{-3}$ M

Trimethylaluminum . . . . . $13.72 \times 10^{-3}$ M

[a] Calculated from Equation (5)

Table 19. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $10^4 k'$,[a] $sec^{-1}$ |
|---|---|---|
| 55 | 1.034 | |
| 1005 | 0.939 | 2.09 |
| 2015 | 0.900 | 1.72 |
| 3000 | 0.839 | 1.60 |
| 4008 | 0.771 | 1.82 |
| 5007 | 0.733 | 1.78 |
| 6006 | 0.710 | 1.68 |
| 7009 | 0.695 | |
| 8003 | 0.669 | |
| 12008 | 0.600 | |
| 16031 | 0.535 | |
| 21500 | 0.476 | |
| 86000 | 0.262 | |

Avg. 1.78 ± 0.12

Initial Concentrations

Benzophenone . . . . . $8.15 \times 10^{-3}$ M

Trimethylaluminum . . . . . $8.08 \times 10^{-3}$ M

[a] Calculated from Equation (5)

Table 20. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $10^4 k'$,[a] $sec^{-1}$ |
|---|---|---|
| 60 | 1.061 | |
| 1000 | 0.980 | 1.38 |
| 2006 | 0.913 | 1.65 |
| 4000 | 0.813 | 1.58 |
| 4998 | 0.778 | 1.54 |
| 6000 | 0.749 | 1.49 |
| 10002 | 0.661 | 1.43 |
| 13003 | 0.618 | |
| 17001 | 0.565 | |
| 20000 | 0.540 | |
| 30000 | 0.445 | |

Avg. 1.51 ± 0.07

Initial Concentrations

Benzophenone . . . . . $8.35 \times 10^{-3}$ M

Trimethylaluminum . . . . . $8.28 \times 10^{-3}$ M

[a] Calculated from Equation (5)

Table 21. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $10^4 k'$,[a] $sec^{-1}$ |
|---|---|---|
| 55 | 1.037 | |
| 1000 | 0.960 | 1.61 |
| 3002 | 0.842 | 1.56 |
| 5003 | 0.770 | 1.43 |
| 6005 | 0.737 | 1.42 |
| 6998 | 0.719 | 1.35 |
| 8000 | 0.697 | 1.30 |
| 9997 | 0.658 | 1.29 |
| 15000 | 0.585 | |
| 20000 | 0.535 | |
| 25000 | 0.485 | |

Avg. 1.42 ± 0.09

Initial Concentrations

Benzophenone . . . . . $8.17 \times 10^{-3}$ M

Trimethylaluminum . . . . . $8.28 \times 10^{-3}$ M

[a] Calculated from Equation (5)

Table 22. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $10^4 k'$,[a] $sec^{-1}$ |
|---|---|---|
| 55 | 2.040 | |
| 499 | 1.939 | 2.26 |
| 998 | 1.841 | 2.21 |
| 2000 | 1.682 | 2.18 |
| 4004 | 1.493 | 1.93 |
| 5000 | 1.415 | 1.91 |
| 10003 | 1.165 | 1.97 |
| 15000 | 0.981 | |
| 20003 | 0.830 | |
| 30000 | 0.658 | |
| 40000 | 0.545 | |
| 127000 | 0.479 | |

Avg. 2.08 ± 0.14

Initial Concentrations

Benzophenone . . . . . $16.05 \times 10^{-3}$ M

Trimethylaluminum . . . . . $16.00 \times 10^{-3}$ M

[a] Calculated from Equation (5)

Table 23. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $10^4 k'$,[a] $sec^{-1}$ |
|---|---|---|
| 47 | 1.995 | |
| 993 | 1.817 | 1.98 |
| 2001 | 1.670 | 1.97 |
| 3000 | 1.575 | 1.81 |
| 3991 | 1.465 | 1.89 |
| 4995 | 1.405 | 1.79 |
| 6009 | 1.330 | 1.81 |
| 8006 | 1.214 | 1.87 |
| 12008 | 1.043 | |
| 16003 | 0.920 | |
| 20010 | 0.810 | |
| 86000 | 0.465 | |

Avg. 1.90 ± 0.07

Initial Concentrations

Benzophenone . . . . . $15.71 \times 10^{-3}$ M

Trimethylaluminum . . . . . $15.82 \times 10^{-3}$ M

[a] Calculated from Equation (5)

Table 24. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $k_d$[a] $l\ mole^{-1}\ sec^{-1}$ | $k\sqrt{K_D}$[b] $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ | $k$[c] $l\ mole^{-1}\ sec^{-1}$ |
|---|---|---|---|---|
| 0 | 1.425 | | | |
| 13.3 | 1.226 | 5.14 | .232 | 2.57 |
| 20.5 | 1.107 | 5.48 | .272 | 2.74 |
| 27.3 | 1.034 | 5.56 | .259 | 2.78 |
| 40.5 | 0.962 | 4.82 | .223 | 2.41 |
| 52.8 | 0.915 | 4.80 | .199 | 2.40 |
| 62.8 | 0.880 | 4.70 | .188 | 2.35 |
| 72.4 | 0.861 | 4.44 | | 2.22 |
| 1000 | 0.713 | | | |
| | | Avg. 5.00 ± 0.30 | Avg. .227 ± .024 | Avg. 2.50 ± 0.15 |

Initial Concentrations

Benzophenone[d] . . . . . $11.30 \times 10^{-3}$ M

Trimethylaluminum . . . . . $17.41 \times 10^{-3}$ M

[a] Calculated from Equation (9)

[b] Calculated from Equation (15)

[c] Calculated from Equation (20)

[d] Average of five values

Table 25. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $k_d$[a] $l\ mole^{-1}\ sec^{-1}$ | $k\sqrt{K_D}$[b] $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ | $k$[c] $l\ mole^{-1}\ sec^{-1}$ |
|---|---|---|---|---|
| 0 | 0.963 | | | |
| 16.2 | 0.802 | 5.24 | .241 | 2.62 |
| 23.1 | 0.750 | 5.02 | .238 | .251 |
| 30.6 | 0.702 | 4.90 | .228 | 2.45 |
| 40.0 | 0.665 | 4.82 | .214 | 2.41 |
| 50.1 | 0.647 | 4.32 | .186 | 2.16 |
| 60.3 | 0.580 | 5.16 | .209 | 2.58 |
| 305.9 | 0.463 | | | |
| 600.8 | 0.463 | | | |
| 899.3 | 0.440 | | | |
| | | Avg. 4.90 ± 0.28 | Avg. .219 ± .013 | Avg. 2.45 ± 0.14 |

Initial Concentrations

Benzophenone[d] . . . . . $7.55 \times 10^{-3}$ M

Trimethylaluminum . . . . . $12.64 \times 10^{-3}$ M

[a] Calculated from Equation (9)

[b] Calculated from Equation (15)

[c] Calculated from Equation (20)

[d] Average of ten values

Table 26. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $k_d$[a] $l\ mole^{-1}\ sec^{-1}$ | $k\sqrt{K_D}$[b] $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ | $k$[c] $l\ mole^{-1}\ sec^{-1}$ |
|---|---|---|---|---|
| 0 | 0.960 | | | |
| 16.8 | 0.773 | 5.36 | .262 | 2.68 |
| 25.4 | 0.708 | 5.36 | .252 | 2.68 |
| 36.2 | 0.648 | 4.16 | .236 | 2.08 |
| 46.0 | 0.581 | 5.70 | .248 | 2.85 |
| 56.6 | 0.551 | 5.18 | .238 | 2.54 |
| 65.6 | 0.530 | 5.10 | .213 | 2.55 |
| 75.6 | 0.496 | 5.40 | .196 | 2.70 |
| 698.4 | 0.381 | | | |
| | | Avg. 5.18 ± 0.32 | Avg. .235 ± .017 | Avg. 2.59 ± 0.16 |

Initial Concentrations

Benzophenone[d] . . . . . $7.55 \times 10^{-3}$ M

Trimethylaluminum . . . . . $13.21 \times 10^{-3}$ M

[a] Calculated from Equation (9)

[b] Calculated from Equation (15)

[c] Calculated from Equation (20)

[d] Average of ten values

Table 27. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $k_d$[a] $l\ mole^{-1}\ sec^{-1}$ | $k\sqrt{K_D}$[b] $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ | $k$[c] $l\ mole^{-1}\ sec^{-1}$ |
|---|---|---|---|---|
| 0 | 0.963 | | | |
| 20.4 | 0.719 | 4.22 | .233 | 2.11 |
| 40.4 | 0.560 | 4.62 | .252 | 2.32 |
| 59.0 | 0.466 | 4.72 | .240 | 2.36 |
| 80.9 | 0.388 | 4.80 | .231 | 2.40 |
| 99.3 | 0.339 | 4.60 | .214 | 2.30 |
| 99.8 | 0.321 | 5.28 | .238 | 2.64 |
| 141.4 | 0.274 | 4.68 | .200 | 2.34 |
| 221.7 | 0.169 | 5.58 | .202 | 2.79 |
| | | Avg. 4.82 ± 0.32 | Avg. .226 ± .018 | Avg. 2.41 ± 0.16 |

Initial Concentrations

Benzophenone[d] . . . . . $7.55 \times 10^{-3}$ M

Trimethylaluminum . . . . . $15.15 \times 10^{-3}$ M

[a] Calculated from Equation (11)

[b] Calculated from Equation (17)

[c] Calculated from Equation (22)

[d] Average of ten values

Table 28. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $k_d$[a] $l\ mole^{-1}\ sec^{-1}$ | $k\sqrt{K_D}$[b] $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ | $k$[c] $l\ mole^{-1}\ sec^{-1}$ |
|---|---|---|---|---|
| 0 | 0.960 | | | |
| 15.1 | 0.771 | 3.98 | .216 | 1.99 |
| 26.9 | 0.685 | 3.94 | .223 | 1.97 |
| 49.5 | 0.506 | 4.80 | .248 | 2.40 |
| 50.9 | 0.550 | 3.78 | .200 | 1.89 |
| 73.1 | 0.452 | 4.08 | .205 | 2.04 |
| 103.9 | 0.391 | 3.70 | .179 | 1.85 |
| 151.2 | 0.300 | 3.86 | .170 | 1.93 |
| 196.8 | 0.217 | 4.60 | .183 | 2.30 |
| | | Avg. 4.10 ± 0.30 | Avg. .203 ± .020 | Avg. 2.05 ± 0.15 |

Initial Concentrations

Benzophenone[d] . . . . . $7.55 \times 10^{-3}$ M

Trimethylaluminum . . . . . $15.34 \times 10^{-3}$ M

[a] Calculated from Equation (11)

[b] Calculated from Equation (17)

[c] Calculated from Equation (22)

[d] Average of ten values

Table 29. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $k_d$[a] $l\ mole^{-1}\ sec^{-1}$ | $k\sqrt{K_D}$[b] $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ | $k$[c] $l\ mole^{-1}\ sec^{-1}$ |
|---|---|---|---|---|
| 0 | 1.441 | | | |
| 11.7 | 1.176 | 3.36 | .241 | 1.68 |
| 20.7 | 1.000 | 3.72 | .260 | 1.86 |
| 31.4 | 0.842 | 3.98 | .261 | 1.99 |
| 40.9 | 0.739 | 4.08 | .258 | 2.04 |
| 51.7 | 0.630 | 4.40 | .263 | 2.20 |
| 61.2 | 0.590 | 4.26 | .250 | 2.13 |
| 70.7 | 0.525 | 4.34 | .248 | 2.17 |
| 89.9 | 0.416 | 4.82 | .258 | 2.41 |
| | | Avg. 4.12 ± 0.34 | Avg. .255 ± .006 | Avg. 2.06 ± 0.17 |

Initial Concentrations

Benzophenone[d] . . . . . $11.30 \times 10^{-3}$ M

Trimethylaluminum . . . . . $22.86 \times 10^{-3}$ M

[a] Calculated from Equation (11)

[b] Calculated from Equation (17)

[c] Calculated from Equation (22)

[d] Average of five values

Table 30. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $k_d$[a] $l\ mole^{-1}\ sec^{-1}$ | $k\sqrt{K_D}$[b] $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ | $k$[c] $l\ mole^{-1}\ sec^{-1}$ |
|---|---|---|---|---|
| 0 | 0.726 | | | |
| 15.0 | 0.601 | 4.52 | .245 | 2.26 |
| 32.4 | 0.515 | 4.32 | .218 | 2.16 |
| 45.1 | 0.446 | 4.80 | .220 | 2.40 |
| 56.1 | 0.404 | 4.96 | .221 | 2.48 |
| 83.7 | 0.344 | 4.60 | .195 | 2.30 |
| 100.0 | 0.316 | 4.32 | .193 | 2.16 |
| 124.4 | 0.305 | 3.86 | | 1.93 |
| 150.2 | 0.258 | 4.22 | .163 | 2.11 |
| | | Avg. 4.48 ± 0.26 | Avg. .208 ± .019 | Avg. 2.24 ± 0.13 |

Initial Concentrations

Benzophenone[d] . . . . . $5.68 \times 10^{-3}$ M

Trimethylaluminum . . . . . $11.70 \times 10^{-3}$ M

[a] Calculated from Equation (11)

[b] Calculated from Equation (14)

[c] Calculated from Equation (22)

[d] Average of five values

Table 31. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $k_d$[a] $l\ mole^{-1}\ sec^{-1}$ | $k\sqrt{K_D}$[b] $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ | $k$[c] $l\ mole^{-1}\ sec^{-1}$ |
|---|---|---|---|---|
| 0 | 1.440 | | | |
| 10.2 | 1.150 | 3.54 | .302 | 1.77 |
| 20.5 | 0.922 | 4.26 | .197 | 2.13 |
| 25.4 | 0.810 | 4.66 | .300 | 2.33 |
| 29.7 | 0.772 | 4.04 | .280 | 2.02 |
| 35.7 | 0.660 | 4.34 | .297 | 2.17 |
| 42.0 | 0.604 | 4.26 | .291 | 2.13 |
| 50.7 | 0.516 | 4.36 | .276 | 2.18 |
| 60.7 | 0.442 | 4.72 | .290 | 2.36 |
| 81.2 | 0.317 | 4.76 | .292 | 2.38 |
| | | Avg. 4.32 ± 0.26 | Avg. .281 ± 0.19 | Avg. 2.16 ± 0.13 |

Initial Concentrations

Benzophenone[d] . . . . . $11.30 \times 10^{-3}$ M

Trimethylaluminum . . . . . $25.28 \times 10^{-3}$ M

[a] Calculated from Equation (9)

[b] Calculated from Equation (14)

[c] Calculated from Equation (20)

[d] Average of five values

Table 32. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $k_d$[a] $l\ mole^{-1}\ sec^{-1}$ | $k\sqrt{K_D}$[b] $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ | $k$[c] $l\ mole^{-1}\ sec^{-1}$ |
|---|---|---|---|---|
| 0 | 0.959 | | | |
| 19.7 | 0.692 | 3.24 | .238 | 1.62 |
| 25.5 | 0.625 | 3.44 | .244 | 1.72 |
| 34.8 | 0.541 | 3.50 | .241 | 1.75 |
| 43.6 | 0.474 | 3.54 | .240 | 1.77 |
| 54.2 | 0.378 | 4.08 | .265 | 2.04 |
| 66.7 | 0.326 | 3.96 | .253 | 1.98 |
| 75.9 | 0.294 | 3.90 | .248 | 1.95 |
| 87.2 | 0.250 | 4.04 | .238 | 2.02 |
| | | Avg. 3.72 ± 0.30 | Avg. .246 ± .007 | Avg. 1.86 ± 0.15 |

Initial Concentrations

Benzophenone[d] . . . . . $7.55 \times 10^{-3}$ M

Trimethylaluminum . . . . . $18.93 \times 10^{-3}$ M

[a] Calculated from Equation (9)

[b] Calculated from Equation (14)

[c] Calculated from Equation (20)

[d] Average of ten values

Table 33. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $k_d$[a] $l\ mole^{-1}\ sec^{-1}$ | $k\sqrt{K_D}$[b] $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ | $k$[c] $l\ mole^{-1}\ sec^{-1}$ |
|---|---|---|---|---|
| 0 | 0.730 | | | |
| 11.0 | 0.605 | 3.24 | .238 | 1.62 |
| 20.4 | 0.510 | 3.50 | .260 | 1.75 |
| 25.2 | 0.465 | 3.56 | .259 | 1.78 |
| 30.1 | 0.435 | 3.48 | .261 | 1.74 |
| 40.8 | 0.371 | 3.52 | .244 | 1.76 |
| 50.0 | 0.318 | 3.64 | .253 | 1.82 |
| 61.1 | 0.276 | 3.58 | .245 | 1.79 |
| 70.6 | 0.231 | 3.86 | .252 | 1.93 |
| | | Avg. 3.54 ± 0.12 | Avg. .251 ± .008 | Avg. 1.77 ± 0.06 |

Initial Concentrations

Benzophenone[d] . . . . . $5.68 \times 10^{-3}$ M

Trimethylaluminum . . . . . $16.26 \times 10^{-3}$ M

[a] Calculated from Equation (9)

[b] Calculated from Equation (14)

[c] Calculated from Equation (20)

[d] Average of five values

Table 34. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $k_d$[a] $l\ mole^{-1}\ sec^{-1}$ | $k\sqrt{K_D}$[b] $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ | $k$[c] $l\ mole^{-1}\ sec^{-1}$ |
|---|---|---|---|---|
| 0 | 0.960 | | | |
| 17.4 | 0.640 | 3.30 | .282 | 1.65 |
| 19.1 | 0.619 | 3.38 | .272 | 1.69 |
| 28.8 | 0.505 | 3.32 | .270 | 1.66 |
| 39.6 | 0.395 | 3.60 | .280 | 1.80 |
| 50.7 | 0.331 | 3.40 | .293 | 1.70 |
| 60.3 | 0.278 | 3.42 | .268 | 1.71 |
| 76.5 | 0.207 | 3.48 | .264 | 1.74 |
| 98.3 | 0.134 | 3.68 | .272 | 1.84 |
| | | Avg. 3.44 ± 0.10 | Avg. .275 ± .008 | Avg. 1.72 ± 0.05 |

Initial Concentrations

Benzophenone[d] . . . . . $7.55 \times 10^{-3}$ M

Trimethylaluminum . . . . . $22.97 \times 10^{-3}$ M

[a] Calculated from Equation (9)

[b] Calculated from Equation (14)

[c] Calculated from Equation (20)

[d] Average of ten values

Table 35. Reaction of Trimethylaluminum with Benzophenone in Benzene at 25°C. Disappearance of the Carbonyl Maximum at 345 mμ.

| Time Seconds | Absorbance | $k_d$[a] $l\ mole^{-1}\ sec^{-1}$ | $k\sqrt{K_D}$[b] $l^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec^{-1}$ | $k$[c] $l\ mole^{-1}\ sec^{-1}$ |
|---|---|---|---|---|
| 0 | 0.726 | | | |
| 9.5 | 0.591 | 2.78 | .241 | 1.39 |
| 15.5 | 0.517 | 2.92 | .261 | 1.46 |
| 20.3 | 0.450 | 3.26 | .281 | 1.63 |
| 24.6 | 0.400 | 3.36 | .291 | 1.68 |
| 30.4 | 0.358 | 3.30 | .272 | 1.65 |
| 40.3 | 0.276 | 3.50 | .288 | 1.75 |
| 55.8 | 0.196 | 3.58 | .302 | 1.79 |
| | | Avg. 3.24 ± 0.22 | Avg. .276 ± .016 | Avg. 1.62 ± 0.11 |

Initial Concentrations

Benzophenone[d] . . . . . $5.68 \times 10^{-3}$ M

Trimethylaluminum . . . . . $21.38 \times 10^{-3}$ M

[a] Calculated from Equation (9)

[b] Calculated from Equation (14)

[c] Calculated from Equation (20)

[d] Average of five values

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